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Locating and Estimating Air Emissions from Sources of Nickel

Radian Corp., Durham, NC

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16. ABSTRACT

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this to compile available information on sources and emissions of these substances. This document deals specifically with nickel. Its intended audience includes Federal, State and local air pollution personnel and others interested in locating potential emitters of nickel and in making gross estimates of air emissions therefrom.

This document presents information on 1) the types of sources that may emit nickel, 2) process variations and release points that may be expected within these sources, and 3) available emissions information indicating the potential for nickel release into the air from each operation.

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Locating And Estimating Air Emissions From Sources Of Nickel

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office Of Air And Radiation
Office Of Air Quality Planning And Standards
Research Triangle Park, North Carolina 27711

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SECTION 1

PURPOSE OF DOCUMENT

The U. S. Environmental Protection Agency (EPA), States, and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, very little information is available on the ambient air concentrations of these substances or on the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this that compiles available information on sources and emissions of these substances. This document specifically deals with nickel and nickel compounds. Its intended audience includes Federal, State, and local air pollution personnel and others who are interested in locating potential emitters of nickel and making gross estimates of air emissions therefrom.

Because of the limited amounts of data available on nickel emissions, and since the configuration of many sources will not be the same as those described herein, this document is best used as a primer to inform air pollution personnel about (1) the types of sources that may emit nickel, (2) process variations and release points that may be expected within these sources, and (3) available emissions information indicating the potential for nickel or nickel compounds to be released into the air from each operation.

The reader is strongly cautioned against using the emissions information contained in this document to try to develop an exact assessment of emissions from any particular facility. Since insufficient data are available to develop statistical estimates of the accuracy of these emission factors, no estimate can be made of the error that could result when these factors are used to calculate emissions for any given facility. It is possible, in some extreme cases, that orders-of-magnitude differences could result between actual and calculated emissions, depending on differences in source configurations, control equipment, and operating practices. Thus, in situations where an accurate assessment of nickel emissions is necessary, source-specific information should be obtained to confirm the existence of particular emitting operations, the types and effectiveness of control measures, and the impact of operating practices. A source test and/or material balance should be considered as the best means to determine air emissions directly from an operation.

SECTION 2

OVERVIEW OF DOCUMENT CONTENTS

As noted in Section 1, the purpose of this document is to assist Federal, State, and local air pollution agencies and others who are interested in locating potential air emitters of nickel and nickel compounds and making gross estimates of air emissions therefrom. Because of the limited background data available, the information summarized in this document does not and should not be assumed to represent the source configuration or emissions associated with any particular facility.

This section provides an overview of the contents of this document. It briefly outlines the nature, extent, and format of the material presented in the remaining sections of this report.

Section 3 of this document provides a brief summary of the physical and chemical characteristics of nickel, its commonly occurring forms, and an overview of its production and uses. A table summarizes the quantities of nickel consumed in various end uses in the United States. This background section may be useful to someone who needs to develop a general perspective on the nature of the substance and where it is manufactured and consumed.

The fourth section of this document focuses on major industrial source categories that may discharge nickel-containing air emissions. Section 4 discusses the production of nickel and nickel compounds, the use of nickel as an industrial feedstock, and the discharge of nickel from industrial sources due to its being a trace contaminant in fossil fuels. For each major industrial source category described in Section 4, example process descriptions and flow diagrams are given, potential emission points are identified, and available emission factor estimates are presented that show the potential for nickel emissions before and after controls employed by industry. Individual companies are named that are reported to be involved with either the production and/or use of nickel and nickel compounds based on industry contacts and available trade publications. Where possible, the chemical form of nickel emissions is identified as this parameter is important in considerations of health effects.

The final section of this document summarizes available procedures for source sampling and analysis of nickel. Details are not prescribed nor is any EPA endorsement given or implied to any of these sampling and analysis procedures. At this time, EPA has generally not evaluated these methods. Consequently, this document merely provides an overview of applicable source sampling procedures, citing references for those interested in conducting source tests.

This document does not contain any discussion of health or other environmental effects of nickel or nickel-containing compounds, nor does it include any discussion of ambient air levels or ambient air monitoring techniques.

Comments on the contents or usefulness of this document are welcomed, as is any information on process descriptions, operating practices, control measures, and emissions information that would enable EPA to improve its contents. All comments should be sent to:

Chief, Source Analysis Section (MD-14)
Air Management Technology Branch
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

SECTION 3

BACKGROUND

NATURE OF POLLUTANT

Nickel (Ni) is a lustrous white, hard, ferromagnetic metal found in transition group VIII of the Periodic Table. It has high ductility, good thermal conductivity, high strength, and fair electrical conductivity.[1] It constitutes approximately 0.009 percent of the earth's crust, making it the 24th most abundant element.[2] Nickel can achieve several oxidation states including -1, 0, +1, +2, +3, and +4; however, the majority of nickel compounds are nickel +2 species.[1] Nickel does not occur in nature as the pure metal but as a component of other minerals.[2,3] The most prevalent forms of nickel minerals are sulfides, oxides, silicates, and arsenicals. Nickel sulfides, silicates, and oxides are the most important nickel minerals from a mining and natural resource standpoint.[2] The most common nickel sulfide mineral, pentlandite [$(NiFe)_9S_8$], accounts for the majority of the nickel produced in the world.[4,5] Physical constants and properties of nickel are presented in Table 1.[4,6]

Nickel is an important metal because of its marked resistance to corrosion and oxidation in both air and aqueous environments. The corrosive resistance of nickel to caustic soda and other alkalies is excellent, and it is fairly resistant to corrosion by sulfuric acid, hydrochloric acid, and organic acids. Nickel is also relatively resistant to corrosion from exposure to chlorine, fluorine, hydrogen chloride, and molten salts. However, in the presence of a strongly oxidizing acid such as nitric acid, nickel exhibits a poor resistance to corrosion. Other compounds which are corrosive to nickel include oxidizing and nonoxidizing acid salts and oxidizing alkaline salts.

TABLE 1. PHYSICAL PROPERTIES OF NICKEL[4,6]

Property	Value
Molecular Weight	58.71
Crystal Structure	face centered cube
Melting Point, °C	1453
Boiling Point, °C	2732
Density at 20°C, g/cm^3	8.908
Specific Heat at 20°C, kJ/(kg-K)	0.44
Average Coefficient of Thermal Expansion x 10^{-6} per °C	
at 20-100°C	13.3
at 20-300°C	14.4
at 20-500°C	15.2
Thermal Conductivity, W/(m-K)	
at 100°C	82.8
at 300°C	63.6
at 500°C	61.9
Electrical Resistivity at 20°C, μohm-cm	6.97
Latent Heat of Fusion, J/g	297.06
Latent Heat of Vaporization, J/g	6222
Solubility	
in water	insoluble
in slightly dilute nitric acid	soluble
in hydrochloric or sulfuric acid	slightly soluble
Vapor Pressure, mm Hg	
1810°C	1
2057°C	10
2234°C	40
2364°C	100
2603°C	400

Nickel carbonyl [$Ni(CO)_4$] is a colorless or slightly yellow liquid that is formed by the direct combination of metallic nickel and carbon monoxide (CO). The compound is miscible in all proportions with most organic solvents but is essentially insoluble in water. Nickel carbonyl is an extremely volatile compound having a vapor pressure at 20°C (68°F) of 44 kPa. Concentrations of nickel carbonyl in ambient air would tend to settle to ground level before being dispersed because its vapor density is about four times that of air.[7] Some of the more important physical properties of nickel carbonyl are presented in Table 2.[4,7,8] The amount of nickel carbonyl that will form in a particular environment is directly proportional to total pressure and/or carbon monoxide content, and is inversely proportional to temperature.[9] Once nickel carbonyl is formed it tends to remain as the metal carbonyl only in the presence of carbon monoxide. In ambient air nickel carbonyl is relatively unstable and will dissociate to carbon monoxide and nickel metal. The half-life of nickel carbonyl in air has been determined to be about 100 seconds.[10] Because nickel carbonyl readily decomposes at temperatures above 60°C (140°F), it can easily be destroyed by passing the stream through a furnace or other high temperature source. The carbon monoxide is oxidized, leaving only elemental nickel particulate matter to be recovered.

Miscellaneous physical/chemical property data and end use information for several other nickel compounds are presented in Table 3.[8] Because most of these compounds are not produced in large quantities commercially, only limited property data are available. Apart from nickel oxide, most of which is used in metallurgical processes, the most significant nickel compound, both in commercial importance and volume of production, is nickel sulfate ($NiSO_4$).[11] The most widely used form of nickel sulfate is as the single salt, nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$).

TABLE 2. PHYSICAL PROPERTIES OF NICKEL CARBONYL[4,7,8]

Property	Value
Molecular Weight	170.75
Melting Point, °C	-25
Boiling Point, °C	42.6
Density at 25°C, g/cm^3	1.32
Critical Temperature, °C	200
Decomposition Point, °C	>60
Vapor Pressure, kPa	
-23°C	5.3
-15.9°C	7.9
-6°C	13.2
0°C	19.2
10°C	28.7
20°C	44.0
43°C	100.0
60°C	decomposes

TABLE 3. PROPERTY AND USE DATA FOR SEVERAL MISCELLANEOUS NICKEL COMPOUNDS[8]

Compound	Properties	Uses
Nickel Acetate Tetrahydrate, $Ni(C_2H_3O_2)_2 \cdot 4H_2O$	- Green crystalline powder - Boiling point = 16.6°C - Density = 1.74 g/cm^3	- Catalyst production, nickel electroplating, aluminum sealing
Nickel Arsenate, $Ni_3(AsO_4)_2 \cdot 8H_2O$	- Yellowish-green powder - Density = 4.98 g/cm^3 - Highly insoluble in water	- Selective fat-hardening hydrogenation catalyst
Nickel Bromide, $NiBr_2$	- Yellowish-green crystals - Very deliquescent - Melting point = 963°C	- Nickel electroplating
Nickel Carbonate, $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$	- Green, odorless powder - Soluble in acids and ammonium salts	- Catalyst manufacture, colored glass production, electroplating
Nickel Chloride Hexahydrate, $NiCl_2 \cdot 6H_2O$	- Green deliquescent powder - Melting point = 1030°C - Heat of fusion = 142.5 cal/g - Soluble in water	- Nickel electroplating
Nickel Cyanide Tetrahydrate, $Ni(CN)_2 \cdot 4H_2O$	- Highly poisonous - Insoluble in water	- Chemical conversion of acetylene to butadiene
Nickel Fluoride, NiF_2	- Green tetragonal crystals - Sublimes in HF stream above 1000°C	
Nickel Formate Dihydrate, $Ni(HCOO)_2 \cdot 2H_2O$	- Fine green crystals - Decomposes to NiO at 180°C - Density = 2.15 g/cm^3	- Preparation of fat-hardening nickel hydrogenation catalysts
Nickel Hydroxide, $Ni(OH)_2$	- Light-green powder - Extremely insoluble in water - Decomposes at 230°C	- Manufacture of nickel-cadmium batteries

TABLE 3. (CONTINUED) PROPERTY AND USE DATA FOR SEVERAL MISCELLANEOUS NICKEL COMPOUNDS[8]

Compound	Properties	Uses
Nickel Iodide, NiI_2	- Blue-green, very deliquescent crystals - Melting point = 797°C - Density = 5.83 g/cm^3	
Nickel Nitrate, $Ni(NO_3)_2 \cdot 6H_2O$	- Green, deliquescent crystals - Melting point = 56°C - Boiling point = 137°C - Density = 2.05 g/cm^3	- Catalyst and battery manufacture
Nickel Oxide, NiO	- Green-black cubic crystals - Melting point = 1990°C - Density = 6.67 g/cm^3 - Insoluble in water	- Catalyst production, alloy and stainless steel production, nickel salts and specialty ceramics
Trinickel Orthophosphate, $Ni_3(PO_4)_2 \cdot 7H_2O$	- Apple-green plates - Decomposes upon heating - Insoluble in water	- Steel coatings, pigment for oil and water paints
Nickel Sulfate Hexahydrate, $NiSO_4 \cdot 6H_2O$	- Green transparent crystals - Density = 2.03 g/cm^3 - Decomposes above 800°C to NiO and SO_3 - Highly soluble in water and ethanol	- Nickel electroplating, catalyst production
Nickel Subsulfide, Ni_3S_2	- Lustrous, yellowish-bronze metal - Density = 5.82 g/cm^3 - Melting point = 790°C - Insoluble in water - Heat of fusion = 25.8 cal/g	

OVERVIEW OF PRODUCTION AND USE

Nickel Production

Nickel production in the United States is referred to as either primary or secondary, depending on the source of the nickel raw material. Primary nickel production involves the smelting of natural nickel ores or the refining of nickel matte. Secondary nickel production involves the reclamation of nickel metal from nickel-based or non-nickel-based scrap metal. Primary nickel production contributes about 40 percent to the domestic nickel production total, while secondary production is responsible for the remaining 60 percent.

Presently, the only nickel ore mining and processing facility in the United States is operated by the Hanna Mining and Nickel Smelting Company near Riddle, Oregon.[12,13] Operations at this facility have been intermittent since early 1982. Consistent operation of the mine and smelting plant is expected by the beginning of 1984.[14] The nickel ore mined and processed by Hanna is known as garnierite.[13] The Hanna processing facility produces nickel in the form of a ferronickel that is 50 percent nickel and 50 percent iron.[15] Ferronickels produced by foreign operations have nickel contents ranging from 20 to 50 percent.[16]

The Hanna Company pyrometallurgical smelter uses an electric furnace to recover selectively metallic nickel and iron from garnierite ore feed. The garnierite ore, which has been crushed and screened, is melted in an electric furnace where nickel oxides, together with a controlled portion of iron oxide, are selectively reduced by ladle mixing of the molten ore with ferrosilicon. The crude ferronickel that is produced is further refined in an electric furnace and is cast into nickel pigs.[13,15]

Primary nickel is also produced domestically by AMAX Nickel, Inc. as a co-product at its copper-nickel refinery in Braithwaite, Louisiana. In addition to nickel, the plant also produces copper, cobalt, and ammonium sulfate. Approximately 25 percent of total domestic nickel production is attributable to the AMAX refinery.[12] Feed material for the AMAX refinery is not nickel ore but a nickel-copper-cobalt matte that is imported from South Africa, Australia, and New Caledonia.[15] Matte is the name applied to an impure metallic sulfide product obtained from the smelting of sulfides of metal ores such as copper, nickel, and lead. The nickel content of the matte used by AMAX ranges from 40 to 75 percent.[15]

In contrast to the Hanna facility, AMAX uses a hydrometallurgical process to refine their matte feed material.[13,15] In this process, a copper sulfate-sulfuric acid solution is first used to leach the matte concentrates.[13] The leaching step dissolves the majority of the nickel and cobalt components in the matte. The resulting solution is purified and then reacted with hydrogen under high temperature and pressure to reduce and precipitate nickel.[15] The nickel powder produced by this process is about 99 percent pure.[17]

The smelting and refining processes used by Hanna and AMAX produce nickel in forms that can generally be classified into two groups. Group I nickel materials are unwrought nickel with a purity of greater than 98 percent. Materials in this group may be in the form of powder, pellets, briquets, rondelles, and cathodes. Group II nickel materials contain less than 98 percent nickel. Nickel oxide sinter (charge nickel), ferronickel, Incomet, and Inco utility shot and pig make up this group. Nickel salt compounds are produced in much lower quantities and constitute a relatively small portion of the domestic primary nickel market.[16,18]

In the United States the secondary recovery and refining of nickel scrap produces more nickel than ore processing and matte refining sources combined. In 1978 nickel from secondary recovery sources amounted to approximately 53,600 Mg (59,100 tons), or 57 percent of domestic nickel production.[11] The potential for increasing the quantity of nickel produced by secondary means is substantial because only about 40 percent of the available nickel-bearing scrap is currently being recycled. The other 60 percent, in the form of batteries, spent nickel-base catalysts, and scrap metal, is being landfilled.[19,20]

Nickel scrap refining generally involves melting it down in either an electric arc or reverberatory furnace, often in the presence of lime and an alloying agent. The product of the smelting operation is often refined further to produce a higher purity nickel material.[20] Two types of scrap, classified as obsolete and industrial, are used as raw materials in the secondary nickel recovery industry. Obsolete scrap consists of alloys in the form of salvaged machinery, sheet metal, aircraft parts, and discarded consumer goods such as batteries. Industrial scrap refers to turnings, casting wastes, and solids from the manufacturing of alloy products. About 60 percent of the nickel scrap processed by secondary refiners is obsolete scrap.[19] The flow of nickel-bearing scrap through the secondary processing industry is depicted in Figure 1.[12] The basic products of the secondary nickel recovery industry include:

- stainless steels,
- low alloy steels,
- nickel-base alloys,
- copper-base alloys,
- aluminum-base alloys,
- nickel metal, and
- nickel in chemical compounds.

Generally, the nickel product of a scrap recovery facility is used to produce the same type of good from which the scrap was generated. For example, recovered nickel-bearing alloy scrap is used to manufacture new nickel alloys.

Information found in published sources is inconsistent concerning the number of secondary nickel refiners operating in the United States. A range

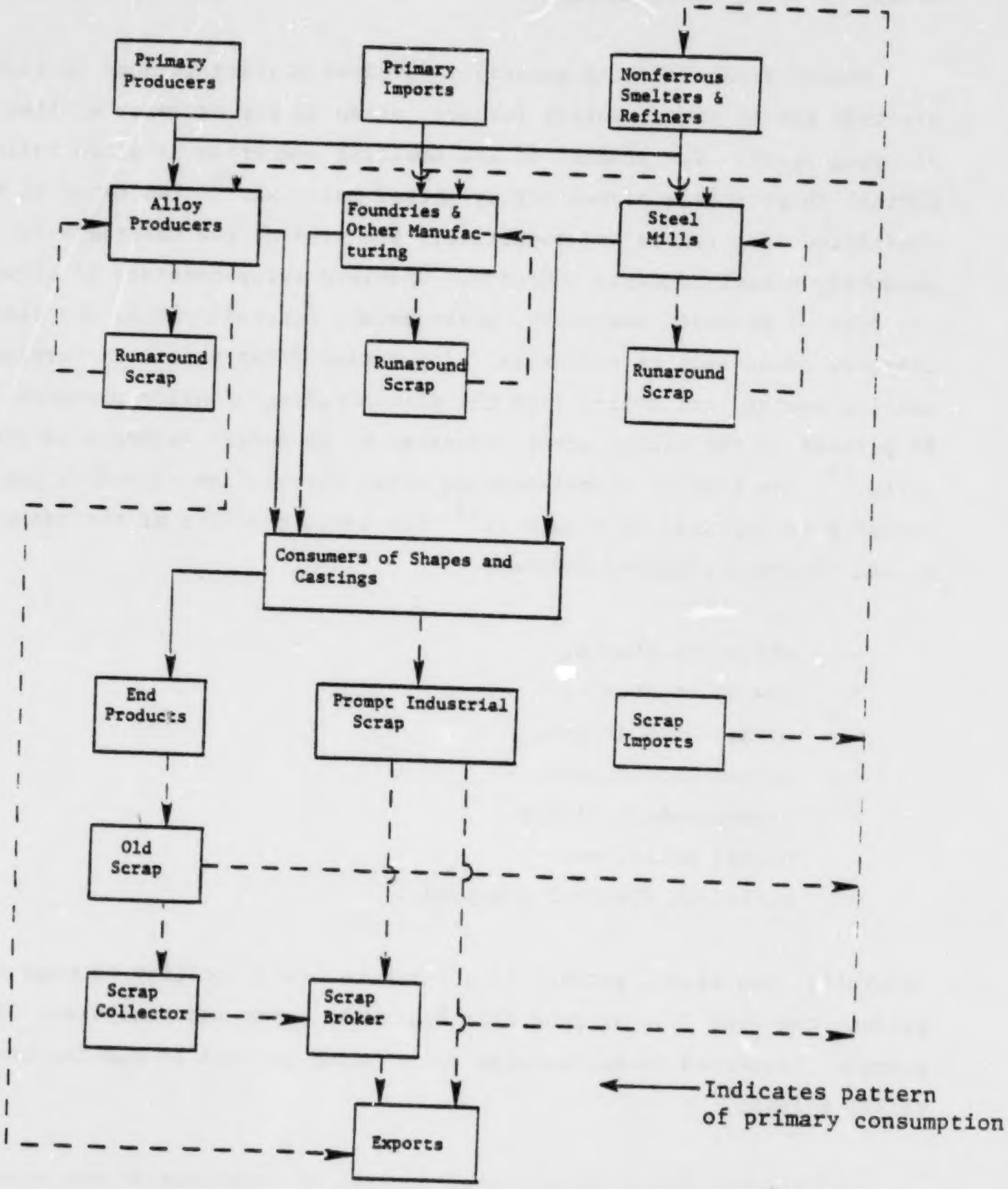
Primary Producers
Primary Imports
Nonferrous Smelters & Refiners
Alloy Producers
Foundries & Other Manufacturing
Steel Mills
Runaround Scrap
Runaround Scrap
Runaround Scrap
Consumers of Shapes and Castings
End Products
Prompt Industrial Scrap
Scrap Imports
Old Scrap
Scrap Collector
Scrap Broker
Exports
Indicates pattern of primary consumption

Figure 1. Nickel scrap flow diagram.[19]

of from 5 to 36 refiners has been indicated.[19-21] The confusion over the total number of refiners appears to have developed because of problems in classifying what constitutes a secondary nickel refiner. Published data of secondary nickel producers have included: (a) firms that process nickel scrap, but do not melt or refine it; (b) firms that produce stainless steel; (c) firms that primarily produce secondary copper; (d) firms that only collect, handle, and transport nickel scrap; (e) firms that melt and/or refine nickel scrap; and (f) firms that produce nickel alloys in a partially refined form. Primary nickel producers, foundries, and other sources that recover their own captive scrap, as well as sources that only handle or transport nickel scrap, are not considered secondary nickel refiners. Table 4 presents a list of firms that have been identified as being secondary nickel refiners.[22,23]

There are other secondary metal recovery facilities, not operated primarily for nickel recovery, that also produce varying quantities of nickel. Secondary copper and secondary aluminum recovery plants are examples of such facilities. Also, because they consume scrap containing varying amounts of nickel, the brass and bronze segments, the cadmium segments, the zinc segments, and the cobalt segments of the secondary metals recovery industry may produce some nickel-bearing materials. In several cases the same facility will recover nickel, aluminum, copper, and other metals. Generally however, a facility is categorized by the type of metal that is produced in the greatest quantity. Table 5 presents a list of facilities that have been reported to be in the secondary copper, aluminum, brass and bronze, cadmium, and cobalt metals recovery industries.[22,23] As shown in the table, several facilities produce more than one metal. Nickel production data for the individual facilities are unavailable. Through their handling and processing of nickel-bearing materials, the facilities listed in Table 5 may potentially emit nickel and nickel compounds to the air.

TABLE 4. COMPANIES IDENTIFIED AS OR THOUGHT TO BE SECONDARY NICKEL REFINERS OR RECLAIMERS[16,22,23]

Company	Location
International Metals Reclamation Co.	Ellswood City, PA
Alloy Metal Products, Inc.	Davenport, IA
American Nickel Alloy Mfg. Co.	New York, NY
Advanced Metals Div. of ARMCO Steel	Baltimore, MD
Belmont Smelting Co.	Brooklyn, NY
Frankel Co.	Detroit, MI
Mercer Alloy Corp.	Greenville, PA
Metal Bank of America, Inc.	Philadelphia, PA
Paragon Smelting Corp.	Long Island City, NY
Riverside Alloy Metal Div. of H. K. Porter Co.	Pittsburgh, PA
I. Schumann Co.	Cleveland, OH
Utica Alloys, Inc.	Utica, NY
Wai Met Alloys Co.	Dearborn, MI
Whitaker Metals-Alloy Div.	Greenville, PA
H. Keamer & Co.	Chicago, IL
R. Lavin & Sons	Chicago, IL
New Jersey Zinc Co.	Bethlehem, PA
National Nickel Alloy Corp.	Pittsburgh, PA
Metallurgical International, Inc.	Cartaret, NJ
American Nickel Alloy Mfg. Co.	Weehawken, NJ
International Wire Products	Wyckoff, NJ
Nassau Smelting & Refining Co.	Tottenville, NY
Niagara Falls Metals & Minerals, Inc.	Buffalo, NY

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of nickel emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

TABLE 5. LIST OF FACILITIES REPORTED TO BE IN THE SECONDARY COPPER, ALUMINUM, BRASS AND BRONZE, CADMIUM, AND COBALT RECOVERY INDUSTRIES[16,22-24]

Company	Location	Secondary Recovery Segment Copper	 Aluminum	 Brass & Bronze	 Cadmium	 Cobalt	 Zinc
Barth Smelting Corp.	Newark, NJ	+		+			
Batchelder-Blasius, Inc.	Spartanburg, SC	+	+				
Bay State Refining, Inc.	Chicopee Falls, MA	+					
Joseph Behr & Sons, Inc.	Rockford, IL	+	+		+		
Belmont Smelting & Refining Works	Brooklyn, NY	+	+		+		
W.J. Bullock, Inc.	Fairfield, AL	+	+	+			
Cepro Corporate Brass Co.	Cleveland, OH	+		+			
Circuit Foil Corp.	Bordentown, NJ	+					
Colonial Metals Co.	Columbia, PA	+	+	+			
General Copper & Brass Co.	Philadelphia, PA	+		+			
Samuel Greenfield Co., Inc.	Brooklyn, NY	+					
Holstead Metal Parts, Inc.	Zelienople, PA	+					
Benjamin Harris & Co.	Chicago Hgts, IL	+		+			
Henning Brothers & Smith	Brooklyn, NY	+	+	+			
K. Hettleman & Sons, Div. of Minerals & Chem.	Baltimore, MD	+		+			+
Holtzman Metal Co.	St. Louis, MO	+	+	+			+
H. Kramer & Co.	Chicago, IL	+		+			
Metal Bank of America, Inc.	Philadelphia, PA	+	+	+			
Nassau Smelting and Refining Co.	Tottenville, NY	+		+			+
Phelps Dodge Refining Corp.	New York, NY	+		+			
Riverside Alloy Metal Div. of H.K. Porter Co.	Pittsburgh, PA	+		+			
Roessing Bronze Co.	Pittsburgh, PA	+		+			

TABLE 5. (CONTINUED) LIST OF FACILITIES REPORTED TO BE IN THE SECONDARY COPPER, ALUMINUM, BRASS AND BRONZE, CADMIUM, AND COBALT RECOVERY INDUSTRIES[16,22-24]

Company	Location	Secondary Recovery Segment Copper	 Aluminum	 Brass & Bronze	 Cadmium	 Cobalt	 Zinc
I. Schumann & Co.	Cleveland, OH	+	+	+			+
M. Seligman & Co.	Chicago, IL	+	+	+			
SIPI Metals Corp.	Chicago, IL	+		+			+
U.S. Metals Refining Co.	New York, NY	+					
R. Lavin & Sons	Chicago, IL	+	+	+			
Cerro Copper Products, Inc.	Saget, IL	+					
Chicago Extruded Metals Co.	Cicero, IL	+		+			
North Chicago Smelting & Refining	North Chicago, IL	+					+
Alloy Metals, Inc.	Troy, MI	+					
Liberman and Glittlen Metal	Grand Rapids, MI	+		+			
Canton Smelting & Refining Co.	Canton, OH	+					
Chase Brass & Copper Co.	Euclid, OH	+		+			
The Federal Metal Co.	Bedford, OH	+		+			
The River Smelting & Refining Co.	Cleveland, OH	+					
North American Smelting Co.	Wilmington, DE	+	+	+			+
Lee Brothers, Inc.	Anniston, AL	+		+			
Revere Copper & Brass, Inc.	Scottsboro, AL	+		+			
Hyman Viener & Sons	Richmond, VA	+	+	+			
New Jersey Zinc Co.	Bethlehem, PA	+		+	+		+
Whittaker Metals	Greenville, PA						
Franklin Smelting & Refining Co.	Philadelphia, PA	+		+			

TABLE 5. (CONTINUED) LIST OF FACILITIES REPORTED TO BE IN THE SECONDARY COPPER, ALUMINUM, BRASS AND BRONZE, CADMIUM, AND COBALT RECOVERY INDUSTRIES[16,22-24]

Company	Location	Secondary Recovery Segment Copper	Aluminum	Brass & Bronze	Cadmium	Cobalt	Zinc
Paragon Smelting Corp.	Long Island City, NY	+	+				
International Wire Products	Wyckoff, NJ	+					
Federated Metals	Newark, NJ	+	+	+			+
Semi-Alloys, Inc.	Mt. Vernon, NJ	+	+	+			
Rochester Smelting & Refining	Rochester, NY	+		+			
Alloys & Chemicals Corp.	Cleveland, OH		+				
Aluminum Billets, Inc.	Youngstown, OH		+				
Aluminum & Magnesium, Inc.	Sandusky, OH		+				
Aluminum Smelters, Inc.	New Allen, CT		+				
Aluminum Smelting & Refining Co.	Maple Hgts, OH		+				
Aurora Refining Co.	Aurora, IL		+				+
Barnum Smelting Co.	Bridgeport, CT		+				
Bay Billets, Inc.	Sandusky, OH		+				
J.R. Elkins, Inc.	Brooklyn, NY		+				
Excel Smelting Corp.	Memphis, TN		+				
Firth Sterling, Inc.	Pittsburgh, PA		+				+
General Smelting Co., Div. of Wabash Smelting, Inc.	Philadelphia, PA		+				+
Gettysburg Foundries	Gettysburg, PA		+				
Hall Aluminum Co.	Chicago Hgts, IL		+				

TABLE 5. (CONTINUED) LIST OF FACILITIES REPORTED TO BE IN THE SECONDARY COPPER, ALUMINUM, BRASS AND BRONZE, CADMIUM, AND COBALT RECOVERY INDUSTRIES$^{16,22-24}$

Company	Location	Secondary Recovery Segment Copper	Aluminum	Brass & Bronze	Cadmium	Cobalt	Zinc
Harco Aluminum, Inc.	Chicago, IL		+				
Northwestern Metal Co.	Lincoln, NE		+	+			
Pioneer Aluminum, Inc.	Los Angeles, CA		+				
George Sall Metals Co.	Philadelphia, PA	+	+	+			
Siberline Manufacturing Co.	Langsford, PA		+				
Sonken-Galamba Corp.	Kansas City, KS		+	+			
Superior Industries, Inc.	Youngstown, OH		+				+
U.S. Aluminum Corp. of Pennsylvania	Marietta, PA		+				
U.S. Reduction Co.	East Chicago, IN		+				
Wabash Smelting, Inc.	Wabash, IN		+				
Allied Metals Co.	Chicago, IL		+				
Precision Extrusions, Inc.	Bensenville, IL		+				
Metropolitan Metal Co.	Detroit, MI		+				
Michigan Standard Alloys	Benton Harbor, MI		+				+
Bohn Aluminum & Brass	Adrian, MI		+	+			+
Union Iron & Metal Co.	Baltimore, MD		+				
Easco Corp.	Baltimore, MD		+				
Ansam Metals Corp.	Baltimore, MD		+	+			+
Tomke Aluminum	Baltimore, MD		+				
Atlantic Metals Corp.	Philadelphia, PA		+				
Aluminum Smelters of New Jersey	Delair, NJ		+				
Niagara Falls Metals & Minerals	Buffalo, NY		+	+			

TABLE 5. (CONTINUED) LIST OF FACILITIES REPORTED TO BE IN THE SECONDARY COPPER, ALUMINUM, BRASS AND BRONZE, CADMIUM, AND COBALT RECOVERY INDUSTRIES[16,22-24]

Company	Location	Secondary Recovery Segment Copper	Aluminum	Brass & Bronze	Cadmium	Cobalt	Zinc
Indium Corp. of America	Edison, NJ		+				
U.S. Metal Products Co.	Erie, PA			+			
Magnolia Metal Co.	Auburn, NE	+		+			
Lewiston Smelting & Refining	Lewistown, PA			+			
Freedman Metal Co.	Brooklyn, NY			+			
Bunting Brass & Bronze Co.	Toledo, OH			+			
Wolverine Metal Co.	Detroit, MI				+		
United Refining & Smelting Co.	Franklin Park, IL			+	+		
Frankel Co., Inc.	Detroit, MI					+	
National Nickel Alloy Corp.	Greenville, PA					+	
Metallurgical International, Inc.	Cartaret, NJ					+	
American Nickel Alloy Mfg. Co.	Weehawken, NJ					+	
Atomergic Chemetals Co.	Carle Place, NY					+	
Alloy Metal Products, Inc.	Davenport, IA					+	+
Max Zuckerman & Sons	Owings Mill, MD					+	
The Himmel Bros. Co.	Hartford, CT		+				
The Platt Bros. Co.	Waterbury, CT						+
Philips Elmet Corp.	Lewistown, ME		+				
Associated Metals Co. of Oakland	Oakland, CA		+				
Chemalloy Electronics	Santee, CA		+				
Globe Metals Co.	Oakland, CA		+				

TABLE 5. (CONTINUED) LIST OF FACILITIES REPORTED TO BE IN THE SECONDARY COPPER, ALUMINUM, BRASS AND BRONZE, CADMIUM, AND COBALT RECOVERY INDUSTRIES[16,22-24]

Company	Location	Secondary Recovery Segment Copper	Aluminum	Brass & Bronze	Cadmium	Cobalt	Zinc
Goldberg Metal Refining Co.	Gardena, CA		+				
Vulcan Materials	Corona, CA		+				
Tri-Alloys, Inc.	Montclair, CA		+				
M.P. Kirk & Sons	Los Angeles, CA		+				
Pacific Smelting Co.	Torrance, CA						+
Bonanza Aluminum Corp.	Anaheim, CA		+				
Eugene Enterprises	Los Angeles, CA		+				
Thorock Metals, Inc.	Compton, CA		+				
U.S. Reduction Co.	Mira Loma, CA		+				
Zenith Metals, Inc.	Los Angeles, CA		+				
Federated Metals Corp.	San Francisco, CA	+					
Levin Metals Corp.	San Jose, CA		+				
Reynolds Metal Co.	Phoenix, AZ		+				
Hi-Duty Alloys	Seattle, WA		+				
Materials Reclamation Co.	Seattle, WA		+				
R.D. Werner Co.	Greenville, PA		+				
Electric Materials, Inc.	Erie, PA	+					
Johnson Bronze Co.	New Castle, PA	+	+	+			
Metallurgical Products	West Chester, PA	+					
Metchem Research	Bristol, PA						+
Delaware Valley Smelting	Bristol, PA						+
Superior Zinc Company	Bristol, PA						+
Signal Alloy Corp.	Chattanooga, TN						+
Florida Smelting Co.	Jacksonville, FL						+
Southwire Co.	Atlanta, GA	+					
Russell Anaconda Aluminum	Miami, FL		+				
Briel Industrial, Inc.	Shelbyville, KY		+				
H&H Metals Co.	Louisville, KY		+				
Berman Bros., Intl.	Birmingham, AL		+				
Culp Smelting & Refining	Attalla, AL		+				
M. Kimerling & Sons	Birmingham, AL		+				
Bay State Aluminum Co.	Braintree, MA		+				

TABLE 5. (CONTINUED) LIST OF FACILITIES REPORTED TO BE IN THE SECONDARY COPPER, ALUMINUM, BRASS AND BRONZE, CADMIUM, AND COBALT RECOVERY INDUSTRIES[16,22-24]

Company	Location	Secondary Recovery Segment Copper	Aluminum	Brass & Bronze	Cadmium	Cobalt	Zinc
Harry Butler & Co.	Boston, MA	+		+			
New England Smelting Works	Boston, MA			+			
Bay State Smelting	Somerville, MA			+			
Anchor Alloys	Brooklyn, NY		+				+
Badger Aluminum Extrusion Corp.	Brooklyn, NY		+				
White Metal Rolling & Stamp Co.	Brooklyn, NY		+				
Ney Metals	Brooklyn, NY						
Republic Metals	Brooklyn, NY						+
Freecast Alloys	Brooklyn, NY						+
Sitkin Refining & Plumbing	Brooklyn, NY			+			+
Friedman Metal Co.	Brooklyn, NY						
Sidney Kronblum Metals	Brooklyn, NY						+
Hugo Neu & Sons	New York, NY						+
Anton Noll Metals	Long Island City, NY						+
Eastern Alloys, Inc.	Maybrook, NY						+
Kearney Smelting	Belle Mead, PA	+		+			+
Metropolitan Metals, Inc.	Camp Hill, PA		+				
National Aluminum Division	Pittsburgh, PA		+				
Illinois Smelting & Refining	Chicago, IL						
Jordan Co.	Chicago, IL						+
Meadowbrook Corp.	LaSalle, IL						+
Sandoval Zinc Co.	Chicago, IL						+
Chemico Metals Co.	Afton, IL	+					+
Hydrometals, Inc.	Dallas, TX	+					
Gulf Reduction Corp.	Houston, TX		+				
Federated Metals	Houston, TX	+					
International Metal Co.	Sapulpa, OK		+				
Federated Metals	Sand Spring, OK						
Arkansas Aluminum	Hot Springs, AR		+				+
Alcoa	Riverdale, IA		+				

TABLE 5. (CONTINUED) LIST OF FACILITIES REPORTED TO BE IN THE SECONDARY COPPER, ALUMINUM, BRASS AND BRONZE, CADMIUM, AND COBALT RECOVERY INDUSTRIES[16,22-24]

Company	Location	Secondary Recovery Segment					
		Copper	Aluminum	Brass & Bronze	Cadmium	Cobalt	Zinc
Diversified Metals	Hazelwood, MO	+	+				
S-G Metals	Kansas City, KS		+				
Eagle-Picher Industries	Galena, KS						+
American Alloys Corp.	Kansas City, MO		+				
Mackay Smelting Co.	Salt Lake City, UT	+		+			
U.S. Reduction Co.	Russellville, AL		+				
Aluminum Billets, Inc.	Girard, OH		+				
Barmet Industries	Akron, OH		+				
Certified Alloys, Inc.	Maple Heights, OH						+
U.S. Reduction Co.	Toledo, OH		+				
Eagle-Piher Industries	Cincinnati, OH				+		
G.A. Avril Co.	Cincinnati, OH	+		+			
ALCOA	Lafayette, IN		+				
Ireco Aluminum	Plymouth, IN		+				
U.S. Reduction Co.	East Chicago, IN		+				
Wabash Smelting	Wabash, IN		+				
Arco	Detroit, MI						+
City Metals Refining	Detroit, MI						+
Grand Rapids Alloys	Grand Rapids, MI	+					+
Gerox, Inc.	Grand Rapids, MI						+
Gardiner Metal Corp.	Chicago, IL						+
Imperial Smelting Corp.	Chicago, IL						+
Inland Metals Refining	Chicago, IL						+
Clearing Smelting Corp.	Chicago, IL						+
Apex International Alloys, Inc.	Cleveland, OH		+				
	Checotah, OK						
	Bicknell, IN						

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of nickel emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

In addition to primary and secondary nickel production sources, nickel, in the form of nickel sulfate ($NiSO_4$), is generated as a by-product or co-product of copper and platinum metal refining.[12,25] In 1975, 7.5 percent of the total domestic nickel production was obtained from co-production during copper and platinum refining. However, in 1976 the amount of nickel generated as a co-product was insignificant compared to the amount produced by primary nickel smelters and refiners and secondary refiners. There is considerable uncertainty about estimating the level of nickel production achievable from co-production because there is no fixed relationship between the quantities of copper and platinum recovered and the quantity of nickel produced.[12,25] Recent estimates of the amount of nickel produced by this method could not be determined.

Nickel Uses

In 1978 approximately 162,700 Mg (180,700 tons) of nickel were consumed in the United States in a wide variety of producer and consumer goods.[15] Nickel was consumed as pure unwrought nickel, ferronickel, nickel oxide, and nickel salts. The consumption of nickel has two components, an intermediate consumption or use and an end or product use. The major intermediate and end uses of nickel are summarized in Figure 2.[26] The largest intermediate nickel use is in the manufacture of nickel-bearing alloys, including stainless and alloy steels, ductile and cast irons, cupronickels, and high nickel alloys.[18]

Figure 3 presents a summary of the major intermediate uses of nickel on a total weight and percentage basis.[15] Over 80 percent of all intermediate nickel consumption goes into the production of steels and alloys.[15,18] The corrosion resistance, strength, and high ductility of nickel make it a highly valuable alloying element. Nickel alloys such as Monel®, which is about 65 percent nickel and 30 percent copper, are stronger and more corrosion resistant in certain environments than pure nickel, and therefore, are prevalent in applications where extreme temperatures, stress, and

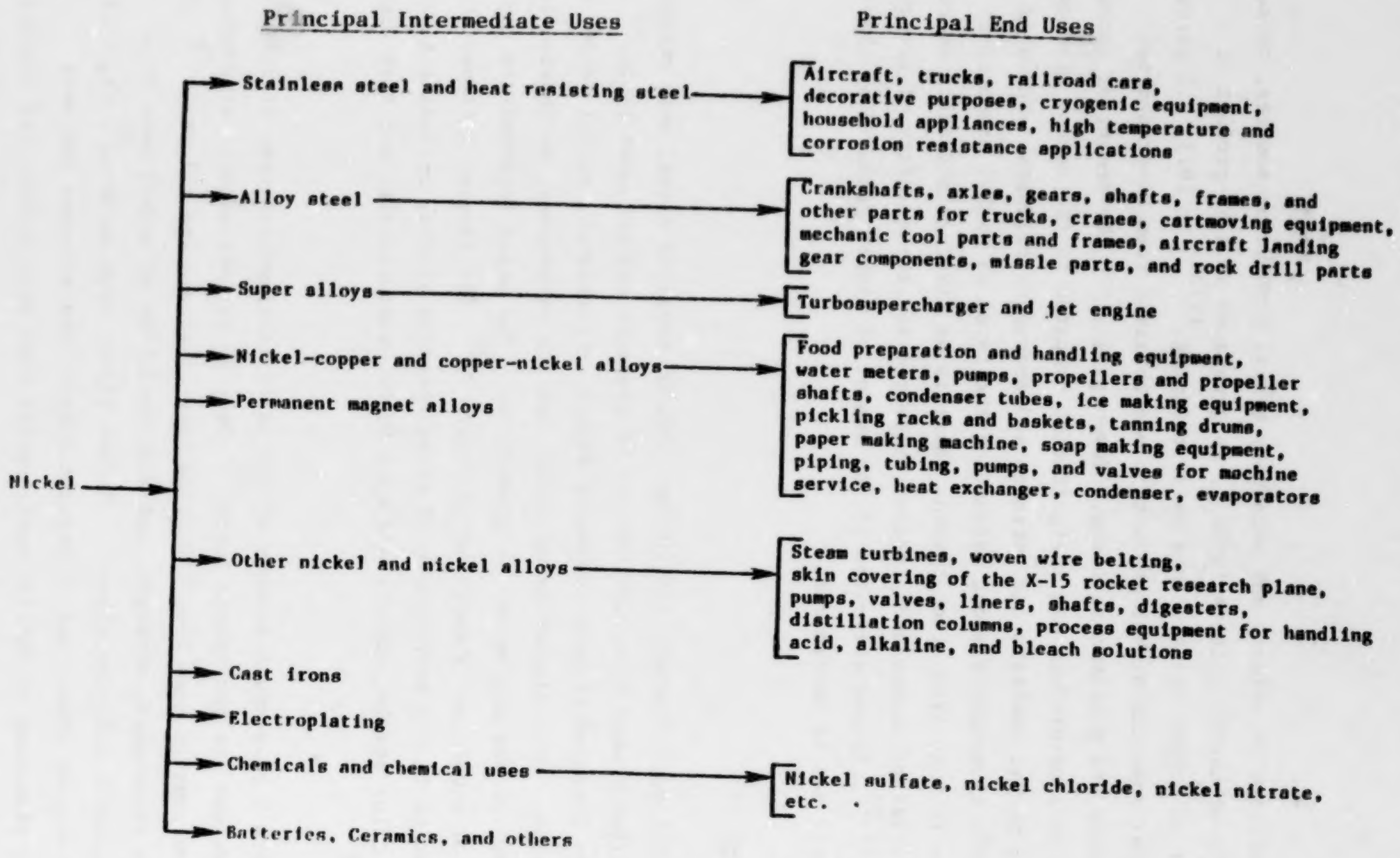
Principal Intermediate Uses
Principal End Uses
Nickel
Stainless steel and heat resisting steel
Aircraft, trucks, railroad cars, decorative purposes, cryogenic equipment, household appliances, high temperature and corrosion resistance applications
Alloy steel
Crankshafts, axles, gears, shafts, frames, and other parts for trucks, cranes, cartmoving equipment, mechanic tool parts and frames, aircraft landing gear components, missle parts, and rock drill parts
Super alloys
Turbosupercharger and jet engine
Nickel-copper and copper-nickel alloys
Food preparation and handling equipment, water meters, pumps, propellers and propeller shafts, condenser tubes, ice making equipment, pickling racks and baskets, tanning drums, paper making machine, soap making equipment, piping, tubing, pumps, and valves for machine service, heat exchanger, condenser, evaporators
Permanent magnet alloys
Other nickel and nickel alloys
Steam turbines, woven wire belting, skin covering of the X-15 rocket research plane, pumps, valves, liners, shafts, digesters, distillation columns, process equipment for handling acid, alkaline, and bleach solutions
Cast irons
Electroplating
Chemicals and chemical uses
Nickel sulfate, nickel chloride, nickel nitrate, etc.
Batteries, Ceramics, and others

Figure 2. Generalized flow pattern for intermediate and end uses of nickel.

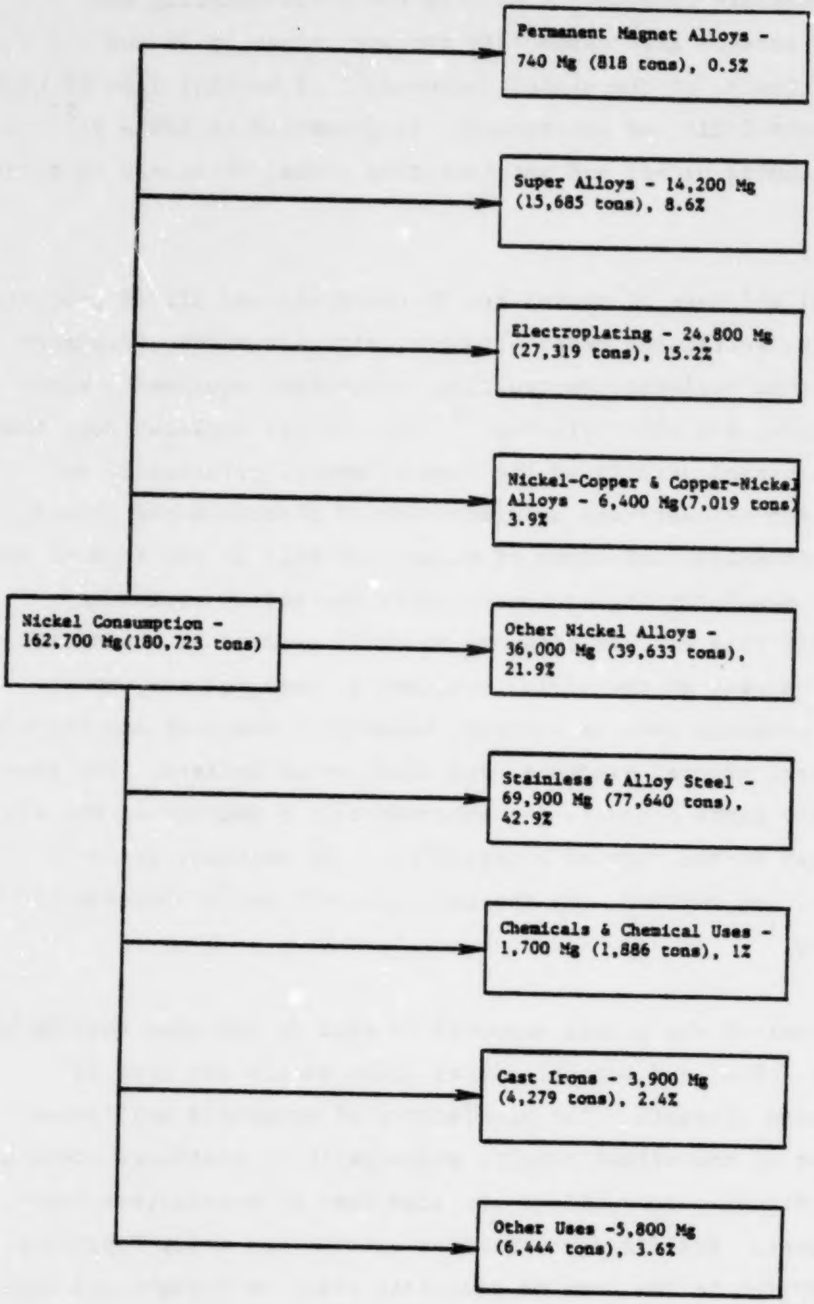
Permanent Magnet Alloys - 740 Mg (818 tons), 0.5%
Super Alloys - 14,200 Mg (15,685 tons), 8.6%
Electroplating - 24,800 Mg (27,319 tons), 15.2%
Nickel-Copper & Copper-Nickel Alloys - 6,400 Mg(7,019 tons) 3.9%
Nickel Consumption - 162,700 Mg(180,723 tons)
Other Nickel Alloys - 36,000 Mg (39,633 tons), 21.9%
Stainless & Alloy Steel - 69,900 Mg (77,640 tons), 42.9%
Chemicals & Chemical Uses - 1,700 Mg (1,886 tons), 1%
Cast Irons - 3,900 Mg (4,279 tons), 2.4%
Other Uses -5,800 Mg (6,444 tons), 3.6%

Figure 3. Intermediate use tree of nickel in 1978.[15]

corrosive substances are found. After metallurgical uses, the most significant intermediate consumption sectors are electroplating and chemicals. These sectors are responsible for approximately 13 and 1 percent, respectively, of the nickel consumed.[15] A partial list of nickel platers, both electrolytic and electroless, is presented in Table 6.[27] A list of firms consuming nickel and manufacturing nickel chemicals is given in Table 7.[28]

The principal end uses of nickel are in chemicals and allied products, petroleum refining, fabricated metal products, aircraft parts, machinery, household appliances, building construction, electrical equipment, motor vehicle construction, and ship building.[12] For end use applications, over 90 percent of all nickel used is in the form of metal, principally in alloys.[12] Petroleum refiners and manufacturers of chemicals and allied products are the principal end users of nickel, chiefly in the form of metal alloys applied in manufacturing equipment parts exposed to corrosive chemicals. In 1978 this end use consumed about 23 percent of the nickel supply. About 9 percent of the nickel consumed is used to manufacture fabricated metal products such as cutlery, handtools, hospital and kitchen equipment, ductwork, general hardware, and sheet metal boilers. The production of aircraft parts accounts for approximately 8 percent of the nickel end uses, primarily in the form of superalloys. Jet engines, turbo-superchargers, and gas turbines are the main aircraft parts composed of nickel superalloys.[12]

About 8 percent of the nickel consumed is used in the construction of general machinery. Cast and wrought nickel alloy steels are used in machinery to provide strength. The manufacture of household appliances consumes 7 percent of the nickel supply, principally in stainless steel and electroplating. Nickel-copper alloys are also used to manufacture food-processing equipment. Building construction constitutes about 9 percent of all nickel consumption in the form of stainless steel or wrought and cast alloy steels. Nickel steels are preferred for structural members because of

TABLE 6. PARTIAL LIST OF FIRMS INVOLVED IN NICKEL PLATING OPERATIONS[27]

Electrolytic Nickel Platers

Avalon Plating Co.	Alhambra, CA
Kotoff & Co., Inc.	El Monte, CA
Electroforms, Inc.	Gardenia, CA
Alco-Cad Nickel Plating Corp.	Los Angeles, CA
Bronze-Way Plating Corp.	Los Angeles, CA
Cad-Nickel Plating Co., Inc.	Los Angeles, CA
General Electroplating	Los Angeles, CA
Precision Gage Plating Co.	Los Angeles, CA
Chrome Nickel Plating Inc.	Lynwood, CA
Continental Plating Co.	Oakland, CA
Haws Plating Works Inc.	Oakland, CA
Lane Metal Finishers, Inc.	Oakland, CA
Pacific Rustproofing Co.	Oakland, CA
California Plating Co., Inc.	San Carlos, CA
Superior Plating Works	San Diego, CA
Van Der Horst Corp.	San Francisco, CA
Oliver Wire and Plating Co.	San Leandro, CA
Ancidite Metal Finishing Div.	Santa Clara, CA
Foss Plating Co.	Santa Fe Springs, CA
Artistic Polishing & Plating	South El Monte, CA
Anadite Metal Finishing Div.	South Gate, CA
Sandia Metal Process Inc.	Van Nuys, CA
Jennings Plating Co.	W. Los Angeles, CA
Emerik, Inc.	Colorado Springs, CO
Chrome Engineering, Inc.	Bridgeport, CT
Bridgeport Plating Co.	Bridgeport, CT
J. B. Coggins Co.	Meriden, CT
Frey Manufacturing Co.	New Britain, CT
Trinacria Specialty Mfg. Co.	Norwich, CT
Whyco Chromium Co.	Thomaston, CT
Summit Finishing Div. of KBI, Inc.	Thomaston, CT
Southeastern Coatings, Inc.	West Palm Beach, FL
Estes Plating Ltd.	Atlanta, GA
Hudson Wire Co.	Trenton, GA
Waynesboro Industries, Inc.	Waynesboro, GA
Braco Industries	Chicago, IL
Claytor Industries	Chicago, IL
Imperial Plating Co.	Chicago, IL
Sigoli Metal Plating Co.	Chicago, IL
API Industries, Inc.	Chicago, IL
American Nickel Works	Chicago, IL
Apollo Metals, Inc.	Chicago, IL
Century Plating Co.	Chicago, IL
Chrome-Rite Co., Inc.	Chicago, IL

TABLE 6. (CONTINUED) PARTIAL LIST OF FIRMS INVOLVED IN NICKEL PLATING OPERATIONS[27]

Electrolytic Nickel Platers	
Elkwood Plating Inc.	Chicago, IL
Gilbertson, Inc.	Chicago, IL
Graham Plating Works	Chicago, IL
Handy Plating Co.	Chicago, IL
James Precious Metals Plating Inc.	Chicago, IL
Mechanical Plating Co.	Chicago, IL
Metcil Plating Co.	Chicago, IL
Modern Plating Corp.	Freeport, IL
American Nickeloid Co.	Peru, IL
Anderson Silver Plating Co.	Elkhart, IN
State Plating Inc.	Elwood, IN
Wayne Metal Protection Co.	Ft. Wayne, IN
Artco Metal Finishing	Goshen, IN
Emconite Division	Indianapolis, IN
G&L Interstate Plating	Mishawaka, IN
Summit Metal Finishing Div. of KBI, Inc.	Mooresville, IN
Delaware Machinery & Tool Co.	Muncie, IN
Richmond Plating Co.	Richmond, IN
Kitchen-Quip, Inc.	Waterloo, IN
Smith Jones, Inc.	Kellogg, IA
Tennis Plating Co., Inc.	Sioux City, IA
Production Plating, Inc.	Lexington, KY
American Plating & Mfg. Co.	Louisville, KY
Louisville Metal Treating Service	Louisville, KY
A-1 Plating Co.	Baltimore, MD
Davis & Hemphill Inc.	Elkridge, MD
D. L. Bromwell, Inc.	Hyattsville, MD
Abercrombie and Co.	Silver Spring, MD
Amesbury Metal Products Corp.	Amesbury, MA
Ames Plating Corp.	Chicopee, MA
Haverhill Plating Co.	Haverhill, MA
Globe Nickel Plating Co., Inc.	Malden, MA
Esses Chrome Plating Co.	Methuen, MA
Norretco	Ware, MA
Advance Plating Corp.	Worcester, MA
New England Plating Co., Inc.	Worcester, MA
Barker Metal Corp.	Worcester, MA
Bronson Plating Co.	Branson, MI
Certified Plating, Inc.	Detroit, MI
General Plating Co.	Detroit, MI
Masselink Electroplating Co.	Grand Rapids, MI
M & L Plating Co.	Jackson, MI
Sarvis Mfg. Co.	Lansing, MI

TABLE 6. (CONTINUED) PARTIAL LIST OF FIRMS INVOLVED IN NICKEL PLATING OPERATIONS[27]

Electrolytic Nickel Platers	
Ductile Chrome Process Co.	Livonia, MI
Electro Finishing Indus., Inc.	Oak Park, MI
Petroskey Mfg. Co. Inc.	Petroskey, MI
Plymouth Plating Works	Plymouth, MI
Michigan Plating of Detroit Inc.	Southfield, MI
G&W Manufacturing Co.	Southfield, MI
Silverstone Plating Co.	Ypsilanti, MI
Miller and Son	Belleville, MD
De Troy Plating Works	Independence, MD
Talbot Commercial Plating	Neosho, MO
Doerr Plating Co.	St. Louis, MO
Siegel-Robert Plating Co.	St. Louis, MO
Cleveland Precious Metals	Merrimack, NH
Carlton-Cooke Plating Corp.	Carlstadt, NJ
Cart-Wright Industries	Engelwood, NJ
Astro Electroplating, Inc.	Farmingdale, NJ
E.C. Electroplating, Inc.	Garfield, NJ
Mitronics Products	Gillette, NJ
PWF Corp.	Little Falls, NJ
Alcaro & Alcaro Plating Co.	Montclair, NJ
Theromo National Industries	Newark NJ
New Brunswick Nickel & Chromium Works	New Brunswick, NJ
Orbel Corp.	Phillipsburg, NJ
General Plating Corporation	Trenton, NJ
B&S Engraving Co.	Union, NJ
Marino Polishing & Plating	Brooklyn, NY
Plated Plastic Industries	Brooklyn, NY
Cohan-Epner Co., Inc.	Brooklyn, NY
Control Electro-Sonversion Crop.	Brooklyn, NY
Regent Metal Products Inc.	Brooklyn, NY
Technical Metal Finishing Corp.	Brooklyn, NY
Val-Kro, Inc.	Buffalo, NY
Tonawanda Platers, Inc.	Hamburg, NY
H.M. Quackenbush, Inc.	Herkimer, NY
Sumereau, Eugene Co., & Sons	Huntington Stn., NY
Star Chromium Corp.	Long Island City, NY
Kings Automatic Plating Co.	Maspeth, NY
M. L. Sheldon & Co., Inc.	New York, NY
Spectranome Plating Co., Inc.	New York, NY
Die Mesh Corp.	Pelham, NY
Gibbs Machine Co.	Greensboro, NC
Akron Plating Co.	Akron, OH
Beringer Plating Inc.	Akron, OH
Ashtabula Bow Socket Co.	Ashtabula, OH

TABLE 6. (CONTINUED) PARTIAL LIST OF FIRMS INVOLVED IN NICKEL PLATING OPERATIONS[27]

Electrolytic Nickel Platers	
Lake City Plating Co.	Ashtabula, OH
Ultrakrome, Inc.	Bedford, OH
Auto Sun Products Co.	Cincinnati, OH
Creutz Plating Corp.	Cincinnati, OH
Advance Plating Co.	Cleveland, OH
Manufacturers Plating Co.	Cleveland, OH
Aetna Plating Co.	Cleveland, OH
Koster Plating Co.	Cleveland, OH
Precious Metal Plating Co.	Cleveland, OH
Bron-Shoe Co.	Columbus, OH
Superior Plating Co.	Columbus, OH
Industrial Platers, Inc.	Columbus, OH
Deyton Rust Proof Co.	Columbus, OH
Queen City Mfg. Co.	Dayton, OH
Eastern Plating, Inc.	Hamilton, OH
J. X. Kreizweld Plating Co.	Martins Ferry, OH
Shelby Standard, Inc.	Salem, OH
Moore Chrome Products Co.	Shelby, OH
Troy Sunshade Co.	Toledo, OH
Clayton Plating Co.	Oklahoma City, OK
Garnet Chemical Corp.	Allentown, PA
Multi-flex Spring & Wire Corp.	Clifton Hgts, PA
American Tinning & Galvinizing Co.	Erie, PA
Klein Plating Works, Inc.	Erie, PA
Advance Specialty Co., Inc.	Lansdowne, PA
Krometal Mfg. Corp.	Philadelphia, PA
Philadelphia Rust-Proof Co.	Philadelphia, PA
Pottstown Plating Works, Inc.	Pottstown, PA
Ametek, Inc.	Sellersville, PA
Gibbs Electronics, Inc.	Somerset, PA
Sylvania - GTE	Warren, PA
High Quality Polishing & Plating	Zionsville, PA
Microfin Corp.	E. Providence, RI
Evans Plating Corp.	N. Providence, RI
Induplate, Inc.	N. Providence, RI
Felch-Wehr Co.	Providence, RI
Booth Electrosystems	Greenville, SC
Carolina Plating & Stamping	Greenville, SC
Arrow Plating Co.	Ft. Worth, TX
B&H Plating Co.	Ft. Worth, TX
Texas Precision Plating, Inc.	Garland, TX
Chrome Platers of Houston	Houston, TX
Bronze-Art Casting & Plating Co.	Houston, TX
Schumacher Co., Inc.	Houston, TX

TABLE 6. (CONTINUED) PARTIAL LIST OF FIRMS INVOLVED IN NICKEL PLATING OPERATIONS[27]

Electrolytic Nickel Platers	
Lubbock Plating Works	Lubbock, TX
Kaspar Electroplating Corp.	Shiver, TX
Vermont Plating, Inc.	Rutland, VT
Alexandria Metal Finishers Inc.	Alexandria, VA
Royal Silver Mfg. Co., Inc.	Norfolk, VA
Allimac Stamping Co., Inc.	Petersburgh, VA
Heath Tecna Corp., Plating Div.	Kent, WA
Asko Processing, Inc.	Seattle, WA
ABC Metal Finishing Co.	Seattle, WA
Alpine Plating Co.	Tacoma, WA
Huntington Plating Inc.	Huntington, WV
Oconomowac Electroplating Co.	Ashippun, WI
Acme Galvanizing, Inc.	Milwaukee, WI
Plating Engineering Co.	Milwaukee, WI
Standard Plating Co., Inc.	Milwaukee, WI
Vulcan Lead Products Co.	Milwaukee, WI
Wacho Mfg. Co., Inc.	Milwaukee, WI
Electroless	
Plateronics Processing, Inc.	Chatsworth, CA
Mechmetals Corp.	El Segundo, CA
Chemplate Corporation	Los Angeles, CA
Electro-Coatings, Inc.	Moraga, CA
Chem-Nickel Co., Inc.	South Gate, CA
Dixon Hard Chrome, Inc.	Sun Valley, CA
Whyco Chromium Co., Inc.	Thomaston, CT
Mac Dermid, Inc.	Waterbury, CT
Har-Conn. Chrome Co.	W. Hartford, CT
Chromium Industries, Inc.	Chicago, IL
Graham Plating Works	Chicago, IL
Grunwald Plating Co., Inc.	Chicago, IL
Krell Laboratories, Inc.	Chicago, IL
Precision Plating Co., Inc.	Chicago, IL
Musick Plating Inc.	E. St. Louis, IL
Electro-Coatings, Inc.	Maine, IL
Electro Seal Corp.	Chesterton, IN
Ni-Mold, Inc.	Indianapolis, IN
Electro-Coatings, Inc.	Indianapolis, IN
Electro-Coatings, Inc.	Cedar Rapids, IA
Cambridge Plating	Belmont, MA
Hopewood Retinning Corp.	Malden, MA
Advanced Materials Systems, Inc.	N. Attleboro, MA
Fountain Plating Company Inc.	W. Springfield, MA
Plating for Electronics, Inc.	Waltham, MA
Electro-Coatings, Inc.	Benton Harbon, MI
G&W Manufacturing Co.	Southfield, MI

TABLE 6. (CONTINUED) PARTIAL LIST OF FIRMS INVOLVED IN NICKEL PLATING OPERATIONS[27]

Electroless	
Tawas Plating Co.	Tawas City, MI
Modern Hard Chrome Service Co.	Warren, MI
Cleveland Precious Metals	Merrimack, NH
SGL Modern Hard Chrome Service Div. of SGL Industries Inc.	Camden, NJ
Alcaro & Alcaro Plating Co.	Montclair, NJ
Keystone Metal Finishers	Secaucus, NJ
Electro Coatings, Inc.	Woodbury Hgts, NJ
Hardchrome Electro Processing Co.	Brooklyn, NY
Technical Metal Finishing Corp.	Brooklyn, NY
Keystone Corporation	Buffalo, NY
Queens Plating Co., Inc.	Long Island, NY
Metallurgical Processing Corp.	Syosset, NY
Electrolizing Corp. of Ohio	Cleveland, OH
Lubrichrome, Inc.	E. Cleveland, OH
Microfin, Corp.	E. Providence, RI
Cahill Chemical Corp.	Providence, RI
Booth Electrosystems	Greenville, SC
Texas Precision Plating, Inc.	Garland, TX
Bronze-Art Casting & Plating Co.	Houston, TX
Electro-Coatings, Inc.	Houston, TX
Alexandria Metal Finishees, Inc.	Alexandria, VA
Heath Tecna Corp. Plating Div.	Kent, WA
Electro Coatings, Inc.	Milwaukee, WI

NOTE: This list is considered partial because the reference cited does not necessarily contain the name of each facility plating nickel. Because of the number of sources involved, there is no single authority that lists all facilities, therefore, it is probable that more sources exist than are given in the table or that some of those given are no longer in operation.

This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of nickel emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

TABLE 7. LIST OF FIRMS PRODUCING NICKEL CHEMICALS[28]

Chemical	Company	Location
Nickel Acetate	C.P. Chems., Inc.	Sewaren, NJ
	Gulf Oil Corp.	
	Harshaw Chem. Co., subsid.	
	Indust. Chems. Dept.	Cleveland, OH
	The Hall Chem. Co.	Wickliffe, OH
	Harstan Chem. Corp.	Brooklyn, NY
	Richardson-Vicks, Inc.	
	J.T. Baker Chem. Co., subsid.	Phillipsburg, NJ
	The Shepherd Chem. Co.	Cincinnati, OH
Nickel Acetylacetonate	MacKenzie Chem. Works, Inc.	
	MacKenzie INTERVAR	Bush, LA
	The Shepherd Chem. Co.	Cincinnati, OH
Nickel Ammonium Sulfate	McGean Chem. Co., Inc.	Cleveland, OH
Nickel Bromide	The Hall Chem. Co.	Wickliffe, OH
	Harstan Chem. Corp.	Brooklyn, NY
Nickel Carbonate	C.P. Chems., Inc.	Sewaren, NJ
	Gulf Oil Corp.	
	Harshaw Chem. Co., subsid.	
	Indust. Chems. Dept.	Cleveland, OH
	The Hall Chem. Co.	Wickliffe, OH
	McGean Chem. Co., Inc.	Cleveland, OH
	Richardson-Vicks, Inc.	
	J.T. Baker Chem. Co., subsid.	Phillipsburg, NJ
	The Shepherd Chem. Co.	Cincinnati, OH
	Texasgulf Inc.	
	M&T Chems. Inc., subsid.	Carrollton, KY
	United Catalysts Inc.	Louisville, KY
Nickel Carbonyl	Pressure Chem. Co.	Pittsburgh, PA
Nickel Chloride	Allied Corp.	
	Allied Chem. Co.	Claymont, DE
	C.P. Chems., Inc.	Sewaren, NJ
	Gulf Oil Corp.	
	Harshaw Chem. Co., subsid.	
	Indust. Chems. Dept.	Cleveland, OH
	The Hall Chem. Co.	Wickliffe, OH
	Harstan Chem. Corp.	Brooklyn, NY
	McGean Chem. Co., Inc.	Cleveland, OH

TABLE 7. (CONTINUED) LIST OF FIRMS PRODUCING NICKEL CHEMICALS[28]

Chemical	Company	Location
Nickel Chloride	Richardson-Vicks, Inc.	
	J.T. Baker Chem. Co., subsid.	Phillipsburg, NJ
	Texasgulf Inc.	
	M&T Chems. Inc., subsid.	Carrollton, KY
Nickel Dibutyldithiocarbamate	E.I. duPont de Nemours & Co., Inc.	
	Polymer Prod. Dept.	Deepwater, NJ
	R.T. Vanderbilt Co., Inc.	Murray, KY
	Vanderbilt Chem. Corp., subsid.	Bethel, CT
Nickel Di-isobutyldithiocarbamate	R.T. Vanderbilt Co., Inc.	
	Vanderbilt Chem. Corp., subsid.	Murray, KY
Nickel Dimethyldithiocarbamate	R.T. Vanderbilt Co., Inc.	
	Vanderbilt Chem. Corp., subsid.	Murray, KY
Nickel 2-ethylhexonate	Mooney Chems., Inc.	Franklin, PA
	The Shepherd Chem. Co.	Cincinnati, OH
Nickel Fluoborate	Allied Corp.	
	Allied Chem. Co.	Claymont, DE
	C.P. Chems., Inc.	Sewaren, NJ
	Gulf Oil Corp.	
	Harshaw Chem. Co., subsid.	
	Indust. Chems. Dept.	Cleveland, OH
	Harstan Chem. Corp.	Brooklyn, NY
	Pennwalt Corp.	
	Chems. Group	
	Ozark-Mahoning Co., subsid.	Tulsa, OK
	Thiokol Corp.	
	Ventron Div.	
	Alfa Products	Danvers, MA
Nickel Fluoride	Pennwalt Corp.	
	Chems. Group	
	Ozark-Mahoning Co., subsid.	Tulsa, OK
Nickel Formate	The Hall Chem. Co.	Wickliffe, OH
	The Shepherd Chem. Co.	Cincinnati, OH
Nickel Halide	Thiokol Corp.	
	Ventron Div.	
	Alfa Products	Danvers, MA

TABLE 7. (CONTINUED) LIST OF FIRMS PRODUCING NICKEL CHEMICALS[28]

Chemical	Company	Location
Nickel Hexamine Fluoborate	Thiokol Corp. Ventron Div. Alfa Products	Danvers, MA
	McGean Chem. Co., Inc.	Cleveland, OH
Nickel Hydrate	C.P. Chems., Inc.	Sewaren, NJ
Nickel Hydroxide	C.P. Chems., Inc.	Sumter, SC
	The Hall Chem. Co.	Wickliffe, OH
	The Shepherd Chem. Co.	Cincinnati, OH
Nickel Naphthenate	Troy Chem. Corp.	Newark, NJ
Nickel Nitrate	C.P. Chems. Inc.	Sumter, SC
	Gulf Oil Corp. Harshaw Chem. Co., subsid. Indust. Chems. Dept.	Cleveland, OH
	The Hall Chem. Co.	Arab, AL Wickliffe, OH
	McGean Chem. Co., Inc.	Cleveland, OH
	Richardson-Vicks, Inc. J.T. Baker Chem. Co., subsid.	Phillipsburg, NJ
	The Shepherd Chem. Co.	Cincinnati, OH
	United Catalysts Inc.	Louisville, KY
Nickelocene (Dicyclopentadienylnickel)	Pressure Chem. Co.	Pittsburgh, PA
Nickel Oxide, Black	McGean Chem. Co., Inc.	Cleveland, OH
Nickel Oxide, Green	Richardson-Vicks, Inc. J.T. Baker Chem. Co., subsid.	Phillipsburg, NJ
	United Catalysts Inc.	Louisville, KY
Nickel Stearate	The Norac Co., Inc. Mathe Div.	Lodi, NJ
	Witco Chem. Corp. Organics Div.	Chicago, IL
Nickel Sulfamate	Gulf Oil Corp. Harshaw Chem. Co., subsid. Indust. Chems. Dept.	Cleveland, OH
	Harstan Chem. Corp.	Brooklyn, NY

TABLE 7. (CONTINUED) LIST OF FIRMS PRODUCING NICKEL CHEMICALS[28]

Chemical	Company	Location
Nickel Sulfamate	McGean Chem. Co., Inc.	Cleveland, OH
	Texasgulf Inc.	
	M&T Chems. Inc., subsid.	Carrollton, KY Pico Rivera, CA
Nickel Sulfate	ASARCO Inc.	
	Federated Metals Corp., subsid.	Whiting, ID
	C.P. Chems., Inc.	Sewaren, NJ
	Gulf Oil Corp.	
	Harshaw Chem. Co., subsid.	
	Indust. Chems. Dept.	Cleveland, OH
	Harstan Chem. Corp.	Brooklyn, NY
	McGean Chem. Co., Inc.	Cleveland, OH
	Richardson-Vicks, Inc.	
	J.T. Baker Chem. Co., subsid.	Phillipsburg, NJ
	The Standard Oil Co. (Ohio)	
	Kennecott Corp., subsid.	
	Kennecott Minerals Co., subsid.	
	Utah Copper Div.	Salt Lake City, UT
	Kennecott Refining Corp., subsid.	Baltimore, MD
	Texasgulf Inc.	
	M&T Chems. Inc., subsid.	Pico Rivera, CA

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of nickel emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

their high strength-to-weight ratios. Thirteen percent of nickel is used in electrical equipment, primarily in the form of resistance alloys. High permeability nickel alloys and nickel-bearing glass-to-metals seals and transistors account for the remainder of the nickel used in electrical equipment.[12]

Motor vehicle construction consumes 6 - 11 percent of the nickel used in the United States.[12,16] The majority of the nickel used goes into electroplating the vehicle trim. In trucks, vans, and buses, nickel-bearing stainless steel is used to construct body parts, frames, and rocker panels. Because of their resistance to corrosion, nickel alloys, cupronickels, and nickel bronzes are used to build and repair ship hulls, frames, and other parts exposed to saltwater. Approximately 4 percent of total nickel consumption is used in ship building actvities.

The chemical properties of nickel allow it to be used in a variety of other applications including catalysts, batteries, dyes and pigments, and ceramics. Nickel in a finely divided form, known as Raney nickel, can dissolve 17 times its volume of hydrogen. This capability leads to the extensive use of nickel in the hydrogenation of fats and oils. Nickel is used in batteries and fuel cells with iron, cadmium, and zinc, and it is also applied in ceramics to form a bond between enamel and iron. The combined miscellaneous uses of nickel constitute approximately 8 percent of total consumption.[12]

Figure 4 presents a summary of the end use markets for nickel on a total weight and percentage basis.[15]

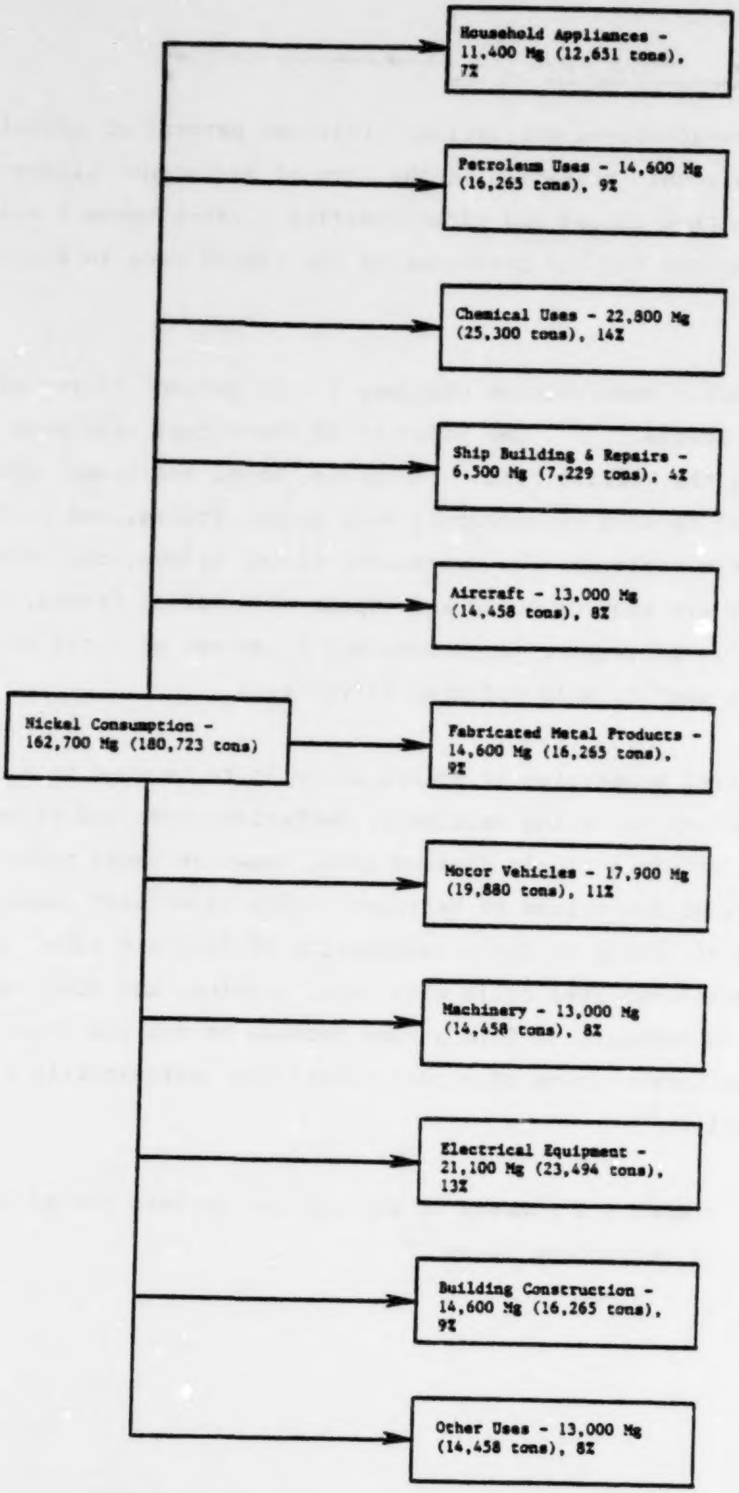
Household Appliances - 11,400 Mg (12,651 tons), 7%
Petroleum Uses - 14,600 Mg (16,265 tons), 9%
Chemical Uses - 22,800 Mg (25,300 tons), 14%
Ship Building & Repairs - 6,500 Mg (7,229 tons), 4%
Aircraft - 13,000 Mg (14,458 tons), 8%
Nickel Consumption - 162,700 Mg (180,723 tons)
Fabricated Metal Products - 14,600 Mg (16,265 tons), 9%
Motor Vehicles - 17,900 Mg (19,880 tons), 11%
Machinery - 13,000 Mg (14,458 tons), 8%
Electrical Equipment - 21,100 Mg (23,494 tons), 13%
Building Construction - 14,600 Mg (16,265 tons), 9%
Other Uses - 13,000 Mg (14,458 tons), 8%

Figure 4. End use applications of nickel in 1978.[15]

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SECTION 4

NICKEL EMISSION SOURCES

Atmospheric nickel emissions occur both from natural and anthropogenic sources.[1] Natural nickel sources include windblown soil and dust, volcanoes, vegetation, forest fires, sea salt, and meteoric dust.[1,2] Estimates of global nickel emissions from natural sources are given in Table 8. These estimates are based on very limited data and should be viewed as order-of-magnitude estimates at best.

Anthropogenic nickel emissions occur from two broad categories of sources: direct and indirect sources. The direct category primarily includes sources that either produce nickel or consume nickel or a nickel compound to manufacture a usable product. The major sources within the direct category are:

- nickel ore mining and smelting,
- nickel matte refining,
- secondary nickel recovery,
- co-product nickel recovery,
- ferrous and nonferrous metals production (nickel alloys and steels, cast irons, stainless steel),
- electroplating,
- battery manufacturing, and
- nickel chemical manufacturing.

Indirect sources are generally those that do not produce nickel or nickel-containing products and only inadvertently handle nickel because it is present as an impurity in a feedstock or fuel. The major indirect nickel sources are as follows:

TABLE 8. GLOBAL EMISSIONS OF NICKEL TO THE ATMOSPHERE FROM NATURAL SOURCES[1,2]

Natural Source	Annual Emissions,[f] 10^3 Mg (10^3 tons)	
Windblown Soil & Dust[a]	20	(22)
Forest Fires[b]	0.6	(0.66)
Volcanoes[c]	3.8	(4.2)
Vegetation[d]	1.6	(1.8)
Sea Salt[e]	0.04	(0.044)
Meteoric Dust	0.18	(0.20)
TOTAL	26.2	(28.8)

[a] Average concentration of nickel in soils was used to determine emissions.

[b] Emissions were calculated assuming average ash content of trees and foliage to be 4% and the average nickel content of the ash is 200 µg/g.

[c] Emissions were calculated assuming average nickel crustal abundance of 75 µg/g and a 5-fold enrichment of nickel in volcanogenic particles.

[d] Emissions were calculated assuming average ash content of vegetative exudates to be 11% and the average nickel content of the ash is 25 µg/g.

[e] Emissions were calculated assuming nickel concentration in ocean water of 210 ng/liter and a nickel enrichment in atmospheric sea salt particles of 200-fold.

[f] Emission numbers are in terms of total nickel.

- coal and oil combustion,
- coke ovens
- municipal refuse and sewage sludge incineration,
- petroleum processing,
- coal conversion processes,
- cement manufacturing,
- coal and oil supplying, and
- asbestos mining.

Indirect sources, primarily coal and oil combustion, are estimated to release from 85 to 94 percent of the total anthropogenic nickel emissions to the air.[3-5]

The following sections briefly describe the operations of both direct and indirect nickel emission sources and the nickel emission points therein. Where available, nickel emission factors are presented for each source. For some sources (e.g., coal liquefaction), atmospheric emissions of nickel have been identified but the quantities have not been determined.

DIRECT SOURCES OF NICKEL

Nickel Production

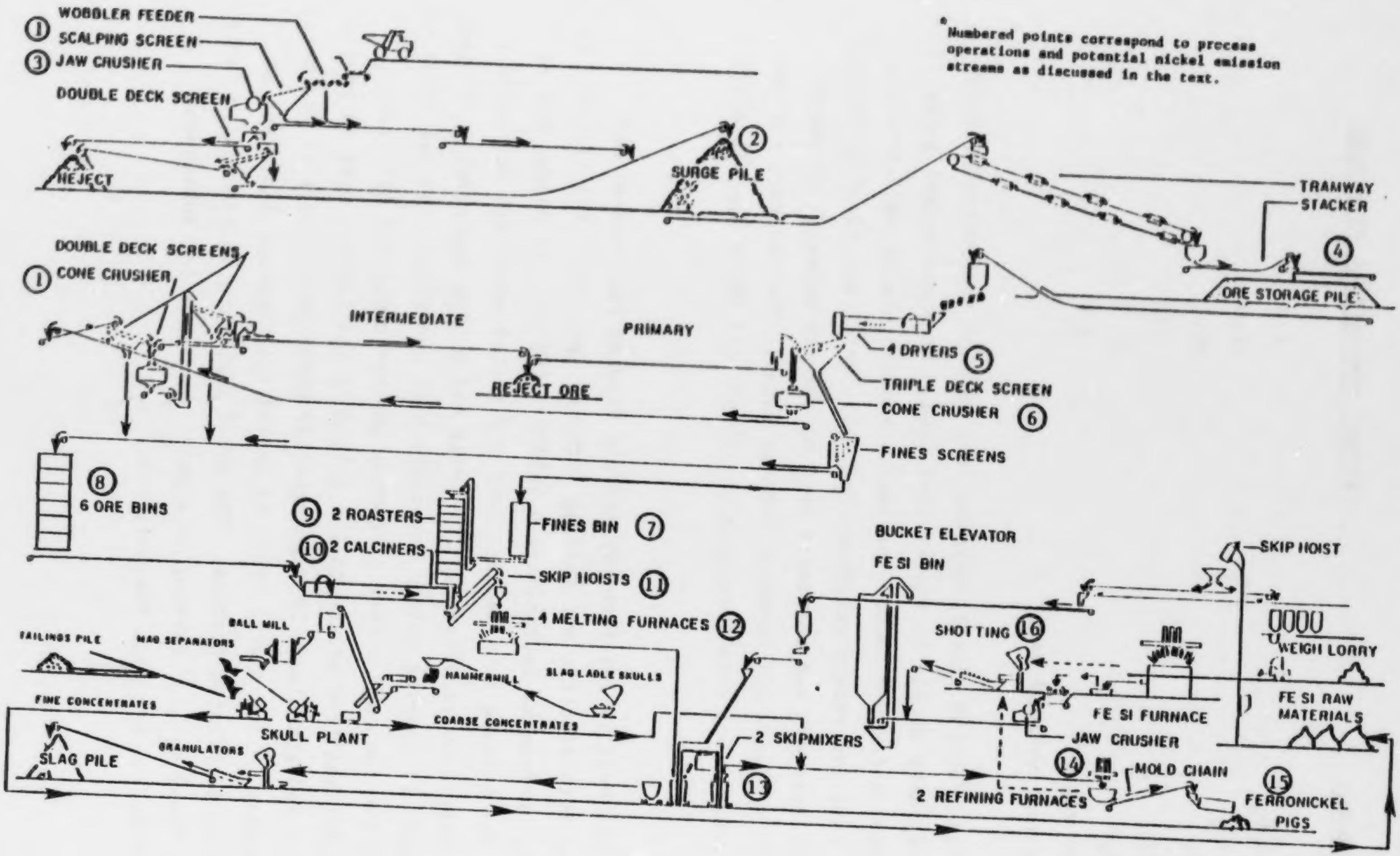
In the United States nickel is generated by three means: nickel ore smelting, the refining of imported nickel matte, and the recovery of nickel from scrap metal. As discussed in Section 3, the majority (60 percent) of domestically produced nickel comes from secondary recovery operations. Matte refining produces approximately 25 percent of the domestic total, with primary nickel ore smelting producing the remaining 15 percent. The processes used in these nickel producing operations, and their resultant nickel emissions, are discussed in detail in the following sections.

Nickel Ore Mining and Smelting

Process Description

The only active nickel mine in the U. S. is located near Riddle, Oregon and is currently operated by the Hanna Mining Company. The raw ore obtained from the mine is known as garnierite, and is approximately 0.96 percent nickel. The nickel content of the ore is expected to decline in future production years. The Hanna Nickel Smelting Company, also located in Riddle, Oregon processes the garnierite to produce a ferronickel containing 50 percent nickel and 50 percent iron. The step-by-step flow of nickel ore from the mine to the final ferronickel product is depicted in Figure 5.[6] The initial step (pt. 1, Figure 5) in the ferronickel process is to screen the raw ore into two fractions. Material less than 14 cm (5.5 in) in diameter is sent directly to a surge pile (pt. 2) and from there on to an ore storage pile (pt. 4). Material greater than 14 cm (5.5 in) is fed to a crusher (pt. 3) and is then screened for a second time. The undersized material from the second screening is carried to the surge pile and from there to the ore storage pile. A belt conveyor delivers the ore from the surge pile to tram cars which empty their contents into an ore storage hopper. Another belt conveyor is used to deliver ore material from the hopper to the ore storage pile. Oversized reject from the second screening (which contains relatively small amounts of nickel) is stockpiled.

The ore material from the storage pile is transferred by front-end loaders into rotary dryers (pt. 5). After drying, the ore is crushed and screened to separate three size fractions (pt. 6). The fines fraction is delivered by belt conveyor to a fines storage bin (pt. 7). Intermediate-sized ore is also delivered by a belt conveyor to six ore storage bins (pt. 8), and oversized ore material is rejected and sent to a stockpile. Fines from the fines storage bin are fed to two vertical roasters (pt. 9) that are fired by natural gas or diesel fuel. The average composition of the feed to the roasters is given below:


① WOBBLER FEEDER
SCALPING SCREEN
③ JAW CRUSHER
DOUBLE DECK SCREEN
REJECT
SURGE PILE ②
TRAMWAY
STACKER
④
ORE STORAGE PILE
DOUBLE DECK SCREENS
① CONE CRUSHER
INTERMEDIATE
PRIMARY
REJECT ORE
4 DRYERS ⑤
TRIPLE DECK SCREEN
CONE CRUSHER ⑥
FINES SCREENS
⑧ 6 ORE BINS
⑨ 2 ROASTERS
⑩ 2 CALCINERS
FINES BIN ⑦
SKIP HOISTS ⑪
4 MELTING FURNACES ⑫
BUCKET ELEVATOR
FE SI BIN
SKIP HOIST
SHOTTING ⑯
WEIGH LORRY
FE SI RAW MATERIALS
FE SI FURNACE
JAW CRUSHER
TAILINGS PILE
MAG SEPARATORS
BALL MILL
HAMMERMILL
SLAG LADLE SKULLS
FINE CONCENTRATES
COARSE CONCENTRATES
SKULL PLANT
SLAG PILE
GRANULATORS
2 SKIPMIXERS
⑬
⑭
MOLD CHAIN
2 REFINING FURNACES
⑮
FERRONICKEL PIGS

*Numbered points correspond to process operations and potential nickel emission streams as discussed in the text.

Figure 5. Flow diagram of the Hanna Nickel Smelting Co. operations.[6]

Component	Percent composition by weight
Al_2O_3	1.9
SiO_2	45.6
Fe	10.1
Ni	1.2
MgO	27
free water	3.2
chemically-bound water	7.3

The figures for iron and nickel represent the percent composition for the total level of these metals in the roaster feed. Iron and nickel actually exist as oxides in the ore feed. Intermediate-sized ore is sent from its storage bins into two rotary calciners (pt. 10), which are fired by natural gas. Both the roasters and calciners heat up the ore material to about 648°C (1200°F) to drive off chemically-bound water. The roasters and the calciners discharge hot ores into skiphoists (pt. 11) which feed into hot ore bins.

Nickel recovery is initiated by gravity feeding the roasted and calcined ores into electric arc melting furnaces (pt. 12). The electric arc melt furnaces operate at approximately 1650°C (3000°F). As molten ore is tapped from the furnace into ladles, iron and nickel metal are extracted by adding a ferrosilicon reductant to the ladle and mixing vigorously. Mixing is accomplished by pouring molten materials back and forth from one ladle to another. As the iron and nickel compounds undergo reduction (pt. 13), metallic nickel and iron settle to the bottom of the ladle. Slag is poured off the ladle and granulated by high pressure water jets. Part of the metal that accumulates in the mixing ladle is poured into another ladle and is transferred to a refining furnace. The metal remaining in the mixing ladle is known as "seed metal," serving as a metal collector for subsequent reactions of molten ore with ferrosilicon.[6]

As molten metal is poured into the refining furnace (pt. 14), refining materials (including dolomite, lime, and fluorspar) are added to the furnace by hand. Chemical reactions between the refining materials and the metals remove impurities from the molten ferronickel. Refined ferronickel is cast into 12.7 kg (28 lb) pigs on a pig casting machine (pt. 15), or is made into shot by pouring the molten material through water jets (pt. 16).[6]

Emission Factors

Emissions of nickel during mining operations are expected to be minimal. Since the water content of the ore is relatively high, about 20 percent, any dust generated would settle quickly and in the vicinity of the source.[7-9] However, as the ore dries in reject or stock piles, increases in fugitive dusts could be observed. The nickel content of such dust would probably average that of the ore, about 0.96 percent.[10] The nickel emitted would be in the form of silicates as in the ore.

In ore smelting the most significant sources of nickel-containing particulate emissions are:

- ore crushers,
- rotary dryers,
- storage and surge bins,
- rotary calciners,
- roasters,
- skiphoists,
- ore melting furnaces,
- the Fe-Si furnace, and
- refining furnaces.

All of these sources are currently controlled by a variety of devices. Fabric filters are used to control emissions from crushers, storage and surge bins, skiphoists, roasters, ore melt furnaces, refining furnaces, and the Fe-Si furnace. Rotary dryer emissions are controlled by first passing the stream through a two-stage cyclone and then onto a wet scrubber. Calciner emissions are being reduced through the use of an electrostatic precipitator (ESP).[11] The efficiencies of these control devices have not been determined by testing; however, the same devices in operation on similar industrial sources have demonstrated efficiencies ranging from 95 to 99 percent.

The quantity of data available to estimate nickel emissions from the Hanna mining and smelting operations is very limited. The most reliable information available appears to be emissions data that have been submitted to the State of Oregon by the Hanna company. These data, which are the results of actual source tests and engineering estimates, are presented in Table 9.[10-12]

Very few data identifying the species or form of nickel emitted during each of the Hanna operations were found in the literature. Based on the types of materials present and the nature of the operations, it seems reasonable to estimate that emissions from crushers will contain nickel as the silicate, as in the ore. Nickel in dusts from dryers and calciners would be present in the silicate mineral lattice because no chemical changes are occurring during these operations. Depending on the temperatures reached during drying and calcining, some nickel on the surface of ore fragments may become oxidized such that some small fraction of nickel may be emitted as an iron-nickel oxide. Nickel oxide or nickel in combination with iron oxide as a ferrite or spinel are probably the dominant species emitted during roasting and melting.[13] Both iron and nickel are transition metals of Group VIII sharing similar properties such as atomic and ionic radii. Both metals also use the same outer electron orbitals when forming complexes such as silicates and oxides and prefer octahedral geometric configurations.[14] Therefore, iron and nickel may be found together in complex oxides. Since roaster feed material may contain about 10 percent iron by weight and temperatures can reach 648°C (1,200°F), it is reasonable to postulate that nickel and iron would be present as an oxide in particulate

TABLE 9. NICKEL EMISSION FACTORS FOR THE PRIMARY SMELTING OF NICKEL ORE[10-12]

Source	Control Device Used	Emission Factor, kg/Mg (lb/ton) of Nickel Produced[a]	
Rotary Dryers[c]			
No. 1	Cyclone/Scrubber	0.28	(0.56)
No. 2	Cyclone/Scrubber	0.26	(0.51)
No. 3	Cyclone/Scrubber	0.26	(0.52)
No. 4	Cyclone/Scrubber	0.021	(0.042)
Crusher House[c]			
No. 1	Fabric Filter	0.006	(0.012)
No. 2	Fabric Filter	0.046	(0.092)
Day Bin[c]			
No. 1	Fabric Filter	0.0009	(0.0019)
No. 2	Fabric Filter	0.0009	(0.0019)
No. 3	Fabric Filter	0.00033	(0.00065)
Calciners[c]	ESP	0.23	(0.46)
Skip Hoists[c]			
No. 1	Fabric Filters	0.034	(0.067)
No. 2	Fabric Filters	0.014	(0.027)
Ore Melter/Roaster[d] Combination			
No. 1	Fabric Filter	0.027	(0.054)
No. 2	Fabric Filter	0.046	(0.092)
Refining Furnace[b,d]	Fabric Filter	0.0065	(0.013)
OVERALL FOR THE PLANT		1.2	(2.4)

---

[a] Emissions expressed as total nickel.

[b] No source test data available, emissions have been estimated.

[c] Nickel emissions from these sources are expected to primarily be in the form of a nickel silicate as in the raw nickel ore.

[d] Nickel emissions from these sources are expected to be in the forms of iron-nickel oxides and ferronickel.

matter. An analysis of the thermodynamics of reactions of nickel-iron oxides and silicates and oxygen shows that at temperatures of 727°-927°C (1,340°-1,700°F), the oxide or silicate is the predominant form.

In speciation studies of particulate matter trapped by control devices during the melting of nickel alloys containing nickel, iron, and chromium (Inconel Alloy 800,840), energy dispersive X-ray analysis (EDXA) of particles revealed patterns which matched those of complex iron-nickel oxides, and to a lesser extent nickel oxide.[15] The ferronickel melt contains both iron and nickel, although not in the same proportions as the alloy. For lack of other data, it seems reasonable to assume that the ferronickel melt would also emit particles containing iron-nickel oxides and nickel oxide.

Nickel Matte Refining

Process Description

The AMAX Nickel Refining Company in Braithwaite, Louisiana is the only facility in the United States that is refining imported matte to produce nickel. In addition to nickel, the AMAX refining process also produces copper, cobalt, and ammonium sulfate. AMAX produces nickel by means of hydrometallurgical refining. A simplified flow diagram of the AMAX operation is presented in Figure 6 and the process is discussed below.[16-18]

To initiate the refining process, the semi-refined nickel-cobalt-copper matte (containing about 40 percent nickel) is crushed to a material less than 1.3 cm (0.5 in) in diameter (pt. 1, Figure 6) and sent to storage bins (pt. 2). A relatively small portion of the crushed matte (about 1300 kg/hr) is drawn off to a sampling area (pt. 3) to analyze and monitor the metal content of the matte.[16] The remainder of the matte is fed to a wet ball mill (pt. 4) where it is ground to minus 200 mesh and then is sent to a thickener and dewatered to 70 percent solids, by weight. The slurry material is then introduced to the atmospheric leaching circuit (pt. 5) of

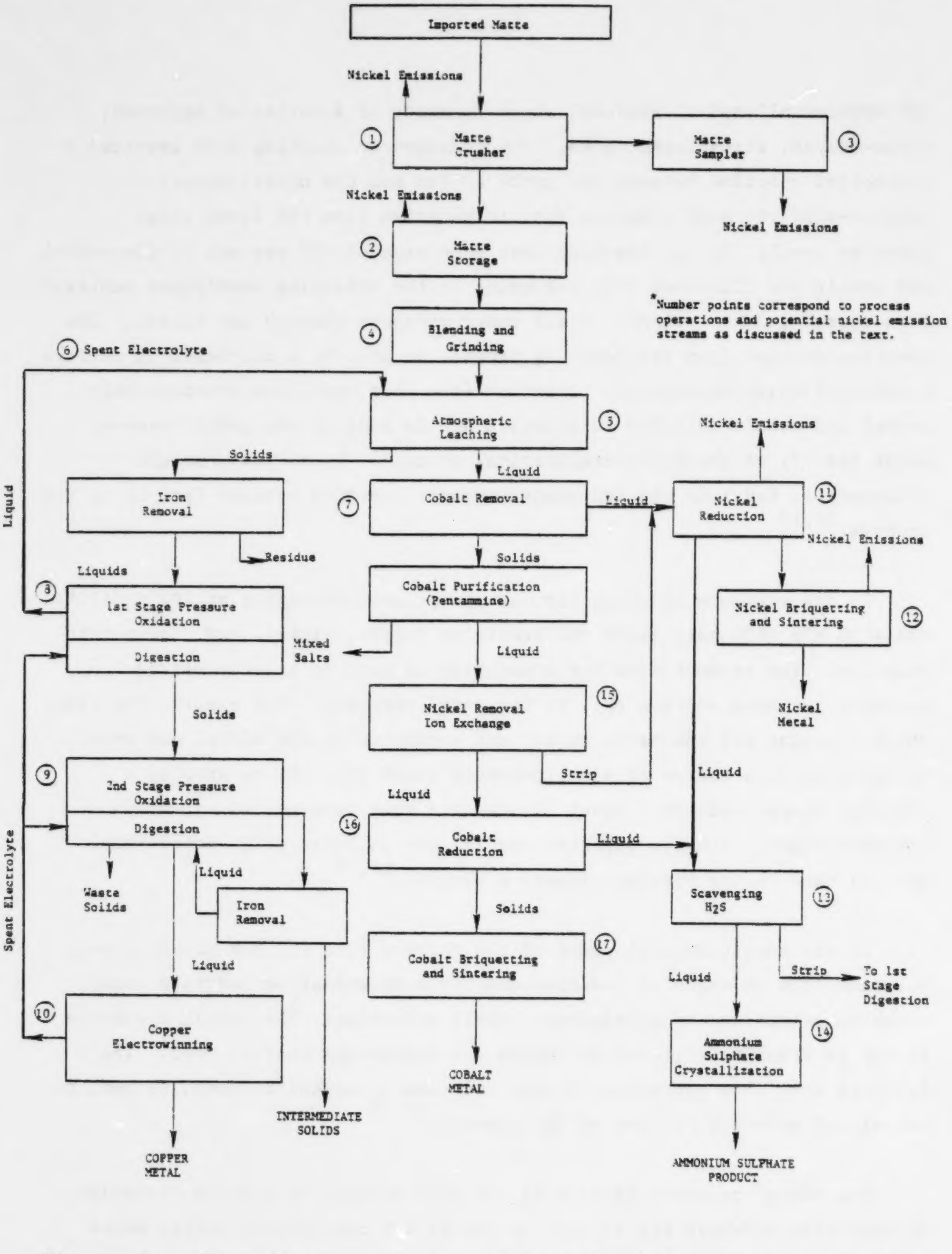

Imported Matte
Nickel Emissions
① Matte Crusher
Matte Sampler ③
Nickel Emissions
Nickel Emissions
② Matte Storage
*Number points correspond to process operations and potential nickel emission streams as discussed in the text.
④ Blending and Grinding
⑥ Spent Electrolyte
Atmospheric Leaching ⑤
Nickel Emissions
Solids
Liquid
Liquid
Iron Removal
⑦ Cobalt Removal
Liquid
Nickel Reduction ⑪
Nickel Emissions
Residue
Solids
Liquids
⑧ 1st Stage Pressure Oxidation
Digestion
Cobalt Purification (Pentammine)
Nickel Briquetting and Sintering ⑫
Mixed Salts
Liquid
Nickel Metal
Solids
Nickel Removal Ion Exchange ⑮
⑨ 2nd Stage Pressure Oxidation
Digestion
Strip
Liquid
Liquid
⑯ Cobalt Reduction
Liquid
Spent Electrolyte
Liquid
Waste Solids
Iron Removal
Solids
Scavenging H2S ⑬
Liquid
Cobalt Briquetting and Sintering ⑰
Liquid
Strip
To 1st Stage Digestion
⑩ Copper Electrowinning
Ammonium Sulphate Crystallization ⑭
COBALT METAL
INTERMEDIATE SOLIDS
COPPER METAL
AMMONIUM SULPHATE PRODUCT

Figure 6. Flow diagram of the AMAX hydrometallurgical nickel refining process.[17,18]

the hydrometallurgical process, which consists of a series of agitated, steam-heated, air-sparged tanks. The atmospheric leaching step requires a controlled reaction between the matte slurry and the nickel/copper sulfate-sulfuric acid solution that is recycled from the first stage pressure leach. In the leaching step approximately 50 percent of the nickel and cobalt are dissolved from the matte by the oxidizing conditions achieved from sparging large volumes of air under pressure through the slurry. The reaction product from the leaching process is sent to a thickener to achieve a solids-liquids separation. Overflow from this operation contains only nickel and cobalt sulfates in solution and is sent to the cobalt removal stage (pt. 7) of the hydrometallurgical process. Underflow from the thickener is fed into the two-stage pressure leaching section (pt. 8) of the process.[17,18]

In the pressure leaching circuit, autoclaves operating at 204°C (400°F) and 4130 kPa (600 psi) leach the remaining copper, nickel, and cobalt into solution. The product from the autoclaves is sent to a second-stage pressure leaching section (pt. 9) for metal recovery. The electrolyte feed, which contains all the matte copper and a portion of the nickel and cobalt, is directed to a series of electrowinning tanks (pt. 10) to produce a finished copper cathode. Spent electrolyte from this operation, which contains nickel, cobalt, unplated copper, and sulfuric acid, is recycled (pt. 6) back to the pressure leaching circuit.[17,18]

At the cobalt removal phase of the process (pt. 7), the nickel-cobalt solution from atmospheric leaching undergoes an oxidation reaction using ammonium persulfate to precipitate cobalt hydroxide. The cobalt hydroxide slurry is pressure filtered to remove the hydroxides in cake form. The filtrate from this operation, a pure solution of nickel sulfate, is sent to the nickel recovery section of the process.[17,18]

The nickel recovery section at the AMAX process is a batch operation.[17] In this step hydrogen gas is used to reduce and precipitate nickel metal from solution. Anhydrous ammonia is used to neutralize the sulfuric acid formed in this process, thereby yielding an ammonium sulfate solution. The precipitated nickel powder is separated by decantation and is then washed, filtered, and dried. The dried powder is then packaged as powder, or is pressed into briquettes and sintered prior to packaging (pt. 12). Residual nickel in the liquor from nickel reduction is sent to a hydrogen sulfide scavenging step (pt. 13) and returned to first stage digestion.[17] Multistage evaporators are then used to produce ammonium sulfate crystals from the purified ammonium sulfate solution.[17,18]

To initiate cobalt metal recovery, the filter cake precipitate from the cobalt removal phase (pt. 7) is first treated with ammonia in an autoclave at 93°C (200°F). This step dissolves the cobalt as an amine complex. All traces of nickel are removed from the cobalt amine solution by acidifying and cooling the solution, thereby yielding nickel double salts, and by subjecting the resulting amine solution to an ion exchange circuit (pt. 15). The purified cobalt solution is directed to a cobalt reduction step (pt. 16) where hydrogenation at elevated temperature and pressure is used to produce cobalt metal. The final cobalt metal product is packaged as a powder or is formed into briquettes (pt. 17).

Emission Factors

In information submitted to the U. S. EPA and to the Louisiana Office of Environmental Affairs, AMAX Nickel lists ten primary sources of nickel emissions from its Braithwaite, Louisiana refinery.[16] These sources, and the type of emission control device applied to each, are delineated in Table 10. Particulate emissions from the majority of sources are collected and removed from the exhaust by a fabric filter.

AMAX has also submitted estimates of total nickel emissions from each of the sources given in Table 10. These estimates are shown in Table 11. Particulate emissions from operations occurring prior to the nickel

TABLE 10. PRIMARY NICKEL EMISSION SOURCES AND CONTROLS AT THE AMAX NICKEL REFINERY[16,18]

Nickel Emission Sources	Source Identification From Figure 6	Control Device Applied and Reported Efficiency
Matte Handling and Hopper Storage	Points 1, 2	Fabric Filter (99.5%)
Matte Sampling Process	Point 3	Fabric Filter (97%)
Laboratory Matte Analysis	Point 3	Fabric Filter (99%)
Matte Crushers	Point 1	Fabric Filter (97%)
Storage Bins	Point 2	Fabric Filter (97%)
Nickel Powder Dryer	Point 11	Cyclone (97%) and Magnetic Filter
Sintering Furnaces	Point 12	Uncontrolled
Briquetting Process	Point 12	Fabric Filter (99%)
Powder Packaging Process	Point 12	Fabric Filter (99.8%)
Fugitive Emissions	Points 11, 12	Fabric Filter (99%)

TABLE 11. ANNUAL NICKEL EMISSIONS FOR THE AMAX NICKEL REFINERY IN BRAITHWAITE, LOUISIANA[18]

Emission Source	Nickel Emissions[a] Mg (tons)/yr
Matte Handling and Hopper Storage[b]	0.64 (0.71)
Matte Sampling Process[b]	0.18 (0.20)
Matte Crushers[b]	0.36 (0.40)
Storage Bins[b]	0.14 (0.15)
Nickel Powder Dryer[c]	0.59 (0.65)
Sintering Furnaces[d]	0.9 (1.0)
Briquetting Process[c]	1.25 (1.39)
Powder Packaging Process[c]	2.4 (2.7)
Fugitive Emissions[c]	0.14 (0.16)
Total Plant	6.6 (7.4)

[a] All emissions estimates are expressed in terms of total nickel.

[b] Nickel emissions from these sources are expected to be in the form of nickel subsulfide (Ni_3S_2).[15,19,20]

[c] Nickel emissions from these sources are expected to be in the form of metallic nickel.[20]

[d] Nickel emissions from this source are expected to be in the forms of metallic nickel and nickel oxide.[19,20]

reduction operation, such as matte handling, sampling, crushing, and storage, contain nickel, copper, and cobalt compounds. AMAX data indicate that the mattes they process contain approximately 40 percent total nickel.[18] Nickel emissions from the matte handling and preparation part of the AMAX facility are expected to be predominantly nickel subsulfide (Ni_3S_2) because the nickel in the sulfide mattes processed is predominantly in this form.[15,19,20] Recent X-ray diffraction tests by AMAX have verified the existence of nickel subsulfide emissions from matte handling operations.[20] Matte handling, crushing, and grinding operations displace nickel subsulfide-containing matte particles that are emitted to the ambient air.

Following the hydrogen reduction nickel precipitation part of the AMAX process, nickel emissions are predominantly in the form of metallic nickel. Nickel emissions from the powder dryer, briquetting process, powder packaging process, sintering furnace, and fugitive sources should be in the form of metallic nickel.[15,19,20] Emissions from the sintering furnace are also likely to contain nickel oxide since some of the input metallic nickel powder is probably oxidized in the sinter furnace.

Potentially a minor amount of nickel carbonyl [$Ni(CO_4)$] could be produced from the hydrogen reduction step of the nickel recovery process at AMAX if carbon monoxide was present as a contaminant in the hydrogen used. Nickel powder and nickel salts have been shown to react to form nickel carbonyl in the presence of carbon monoxide.[21] No information is available on possible carbon monoxide in the process hydrogen or on nickel carbonyl formation and release during nickel precipitation. If nickel carbonyl was formed, it is unlikely that it would eventually be found in ambient air around the plant considering that the half-life of nickel carbonyl in air is only about 100 seconds.[22]

Secondary Nickel Recovery

Process Description

As discussed in Section 3, the secondary nickel scrap recovery industry is a significant component of domestic nickel production. The basic processes conducted at a secondary nickel recovery plant include scrap pretreatment, smelting, refining, and casting of the nickel-based product.[23] All secondary nickel plants do not, however, necessarily use each of these processes. For example, plants receiving relatively clean nickel scrap may not need to carry out a degreasing pretreatment step. The generalized flow pattern of nickel materials through a representative secondary nickel recovery facility is illustrated in Figure 7.[24]

Unless nickel scrap is exceptionally clean and homogeneous when it enters the recovery facility, it must first undergo some degree of pretreatment. Pretreatment generally involves inspecting and sorting the scrap and cleaning or degreasing the scrap. Sorting is performed manually to separate nickel-bearing scrap from non-metallic and non-nickel materials. Pieces of nickel scrap are then segregated with respect to cleanliness and physical form. Clean scrap may be charged directly to the smelting furnace while dirty scrap undergoes degreasing. Nickel scrap is generally degreased by using trichloroethylene solvent. No atmospheric nickel emissions occur during nickel scrap pretreatment.[24,25]

In the smelting step of the recovery process, nickel scrap is either (1) partially purified prior to further refining, or (2) melted with alloying agents to form specific alloys. In either case, the scrap is charged to a furnace, lime is usually added, and the charge is melted. The molten metal is poured into ingot molds or is sent directly into another reactor for refining. Both electric arc and rotary reverberatory furnaces are used to accomplish scrap melting. The effects on the scrap are the same regardless of the furnace type used. Both types of furnaces are sources of

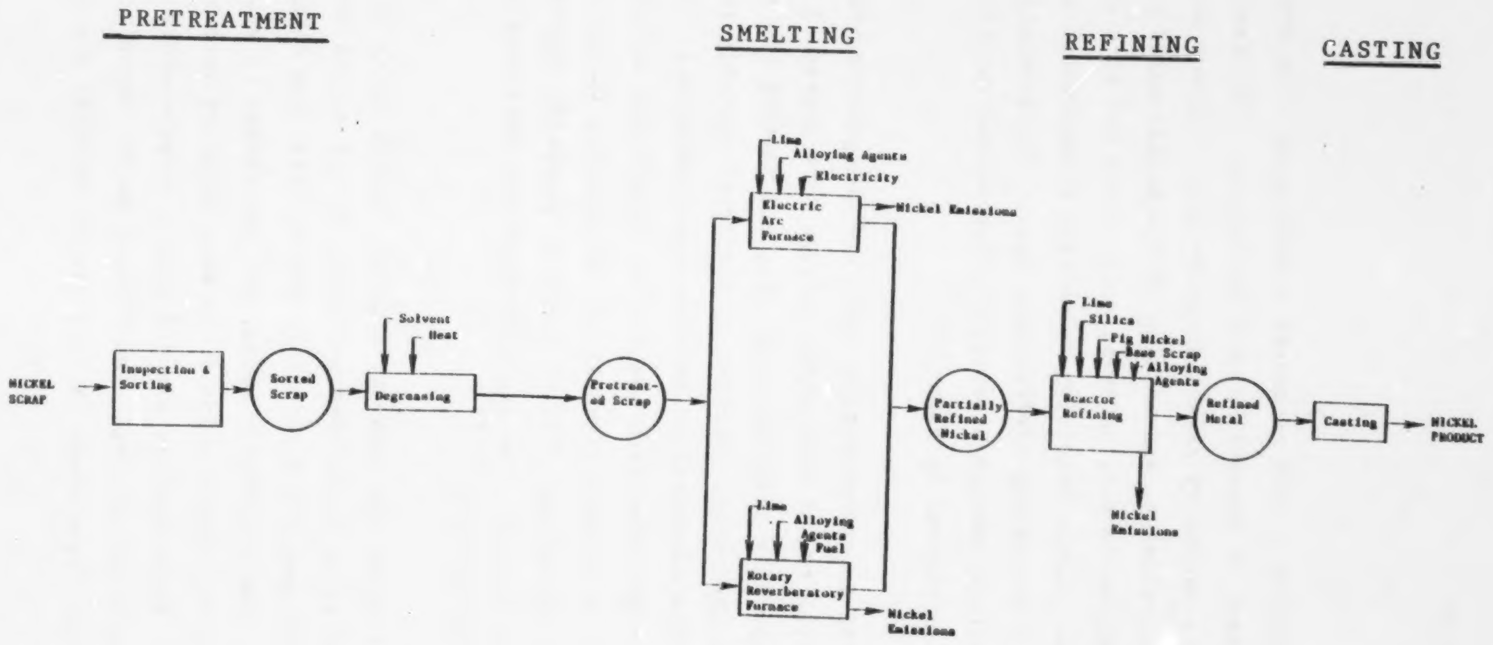

PRETREATMENT
SMELTING
REFINING
CASTING
NICKEL SCRAP
Inspection & Sorting
Sorted Scrap
Solvent
Heat
Degreasing
Pretreated Scrap
Lime
Alloying Agents
Electricity
Electric Arc Furnace
Nickel Emissions
Lime
Alloying Agents
Fuel
Rotary Reverberatory Furnace
Nickel Emissions
Partially Refined Nickel
Lime
Silica
Pig Nickel
Base Scrap
Alloying Agents
Reactor Refining
Nickel Emissions
Refined Metal
Casting
NICKEL PRODUCT

Figure 7. Process flow diagram for a representative secondary nickel recovery plant.[17]

atmospheric nickel emissions, generally in the form of nickel oxide and other more complex forms of oxidized nickel.[19,25] Fabric filter control devices are predominantly used to control the dust emissions from the smelting furnaces.[25]

If higher purity material is required than can be achieved in the smelting furnace, the molten product of smelting is sent to a refining reactor. In the refining reactor, cold base scrap and pig nickel are added to the molten metal. To this mixture are added lime, silica, and specified quantities of alloying metals. The alloying metals (e.g., manganese, titanium, and columbium) are added to produce the required alloy composition. The total charge is then melted and poured into molds. The processes carried out in the refining reactor generate nickel emissions similar to those produced in the smelting step. Fabric filter control devices are routinely used to reduce the release of these emissions into the air.[25]

The final step in the secondary nickel recovery process involves casting the molten product alloys into ingots. After pouring the molten metal into molds, solidification is accomplished by air cooling. The ingot alloys are then removed from the molds and packaged for consumption by the metallurgical industry. Although no atmospheric nickel emissions occur during the casting process, minor amounts of metallic vapor are released into the work environment, which are likely to be oxidized very rapidly.[19,25]

Emission Factors

Emission factors specifically applicable to secondary nickel recovery plants are very limited. The factors that are available apply only to scrap melting furnaces and are presented in Table 12. The accuracy of the factors given in Table 12 has not been determined by testing.

TABLE 12. NICKEL EMISSION FACTORS FOR THE SECONDARY PROCESSING OF NICKEL-BEARING SCRAP[26]

Scrap Source	Emission Factor[a,b]
Stainless Steel[c]	5 kg/Mg (10 lb/ton) of nickel charged[d] or 0.3 kg/Mg (0.6 lb/ton) of steel produced[d]
Nickel Alloy Steels[e]	5 kg/Mg (10 lb/ton) of nickel charged[d]
Iron & Steel Scrap[e]	0.0008 kg/Mg (0.0015 lb/ton) of iron and steel produced[d]
Other Nickel Alloys[f]	1 kg/Mg (2 lb/ton) of nickel charged[d]
Copper Base Alloys[f]	1 kg/Mg (2 lb/ton) of nickel charged[d]
Electrical Alloys[f]	1 kg/Mg (2 lb/ton) of nickel charged[d]
Cast Iron[f]	10 kg/Mg (20 lb/ton) of nickel charged[g]

[a] Nickel is primarily emitted as complex oxides of nickel and other metals.

[b] The emission factors apply to individual melting furnaces.

[c] Emission factor based on questionnaire survey results.

[d] Controlled emission factors. Although specific controls for these factors are not known, the industry generally uses fabric filters for emissions control.

[e] Emission factors based on material balances.

[f] Emission factors based on engineering judgement.

[g] Uncontrolled emission factors.

Source Locations

The locations of firms believed to be engaged in the secondary recovery of nickel metal are given in Table 4 of Section 3.

Other Secondary Metals Recovery Plants

Process Description

Secondary aluminum, copper, cadmium, cobalt, brass and bronze, and zinc recovery facilities have the potential to emit nickel because they process scrap containing varying amounts of nickel. Nickel compounds, probably nickel-containing oxides, are emitted as a minor component of the total particulate emission stream from each of these source categories. Figures 8-13 present flow diagrams that are representative of secondary metal recovery processes performed in the United States. The basic processes involved in all these source categories are so similar that to detail each separately would be repetitive. Generally, there is a scrap pretreatment step, a smelting step, a refining step, and a product casting step.

Typically, scrap metal is brought into the recovery facility, sorted by type, and pretreated according to the physical and chemical nature of the scrap. In zinc recovery plants, for example, pretreatment of scrap can involve crushing and screening, furnace sweating, or sodium carbonate leaching, depending on the nature of the input scrap. In comparison, secondary copper scrap pretreatment can involve crushing and grinding, kiln drying, furnace sweating, or sulfuric acid leaching. As shown in Figures 8-13, similar pretreatment operations exist in all the secondary metals recovery facilities.[27] Atmospheric nickel emissions potentially occur from the pretreatment processes used in the secondary aluminum, copper, brass and bronze, and zinc segments of the metals recovery industry. Wet scrubbers, fabric filters, ESPs and cyclones have been used to control particulate emissions from the various pretreatment processes.[27]

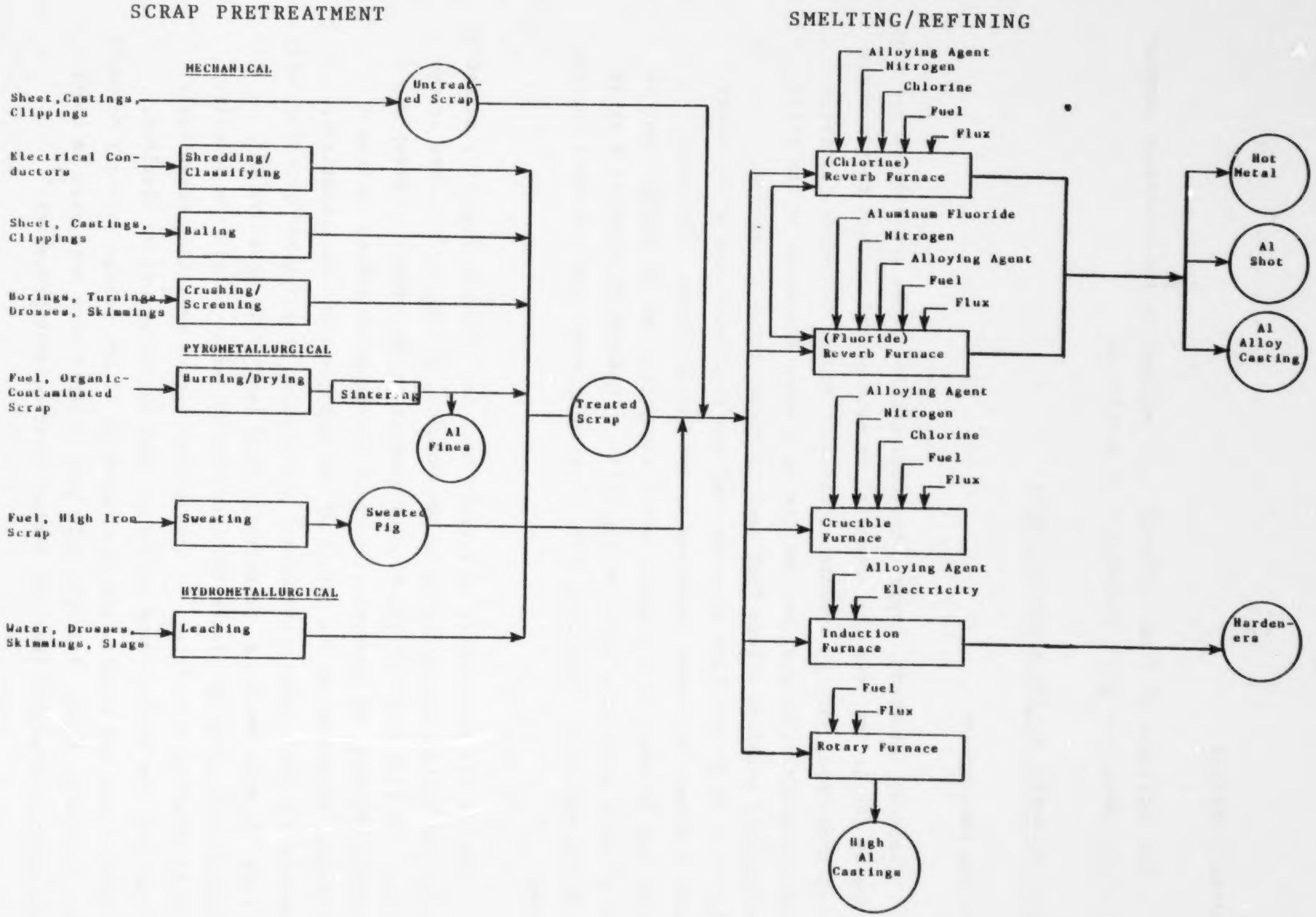

SCRAP PRETREATMENT
SMELTING/REFINING
MECHANICAL
Sheet, Castings, Clippings
Untreated Scrap
Electrical Conductors
Shredding/Classifying
Sheet, Castings, Clippings
Baling
Borings, Turnings, Drosses, Skimmings
Crushing/Screening
PYROMETALLURGICAL
Fuel, Organic-Contaminated Scrap
Burning/Drying
Sintering
Al Fines
Treated Scrap
Fuel, High Iron Scrap
Sweating
Sweated Pig
HYDROMETALLURGICAL
Water, Drosses, Skimmings, Slags
Leaching
Alloying Agent
Nitrogen
Chlorine
Fuel
Flux
(Chlorine) Reverb Furnace
Aluminum Fluoride
Nitrogen
Alloying Agent
Fuel
Flux
(Fluoride) Reverb Furnace
Alloying Agent
Nitrogen
Chlorine
Fuel
Flux
Crucible Furnace
Alloying Agent
Electricity
Induction Furnace
Fuel
Flux
Rotary Furnace
High Al Castings
Hot Metal
Al Shot
Al Alloy Casting
Hardeners

Figure 8. Generalized flow diagram of a secondary aluminum recovery plant.[27]

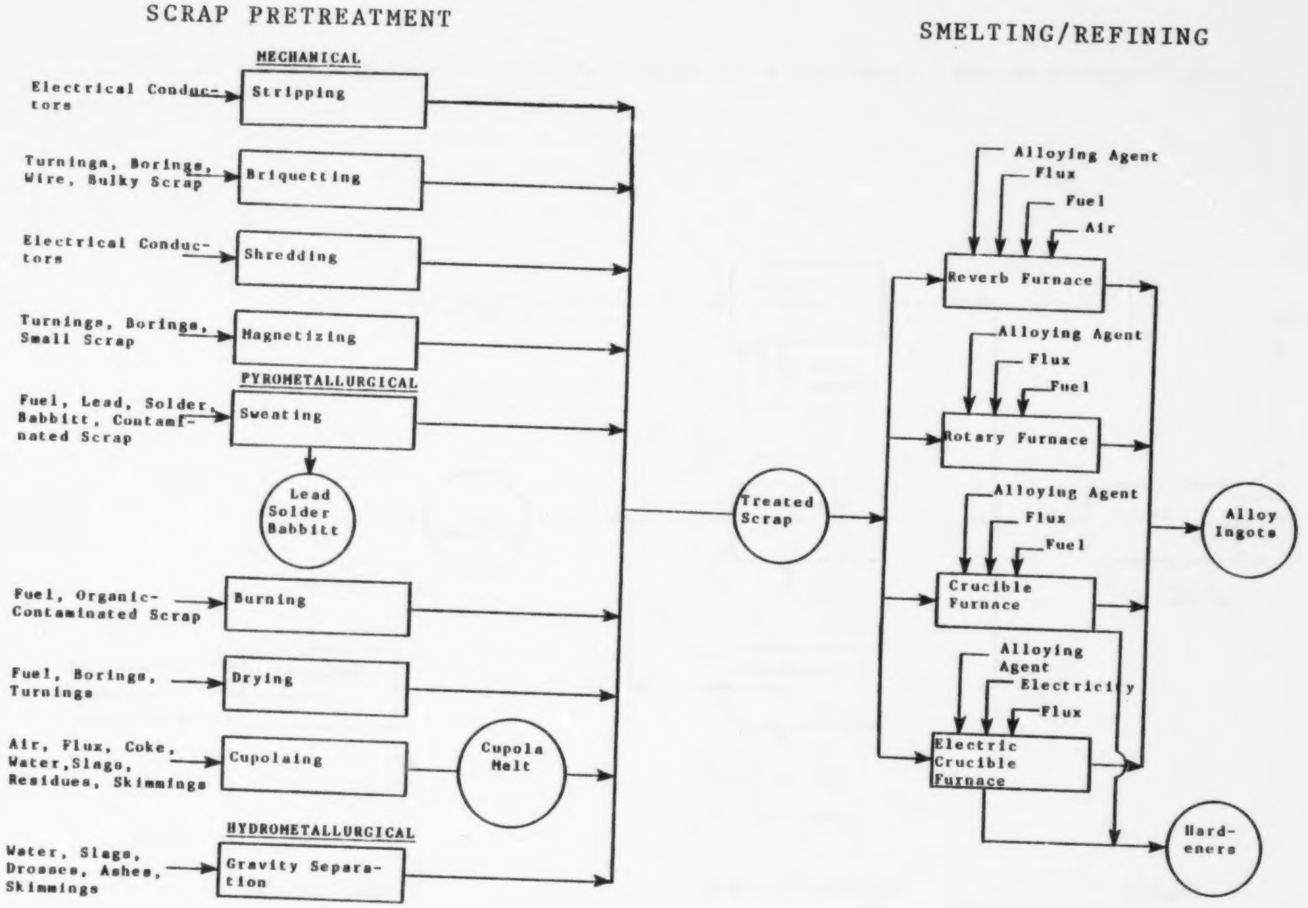

SCRAP PRETREATMENT
SMELTING/REFINING
MECHANICAL
Electrical Conductors
Stripping
Turnings, Borings, Wire, Bulky Scrap
Briquetting
Electrical Conductors
Shredding
Turnings, Borings, Small Scrap
Magnetizing
PYROMETALLURGICAL
Fuel, Lead, Solder, Babbitt, Contaminated Scrap
Sweating
Lead Solder Babbitt
Fuel, Organic-Contaminated Scrap
Burning
Fuel, Borings, Turnings
Drying
Air, Flux, Coke, Water, Slags, Residues, Skimmings
Cupolaing
Cupola Melt
HYDROMETALLURGICAL
Water, Slags, Drosses, Ashes, Skimmings
Gravity Separation
Treated Scrap
Alloying Agent
Flux
Fuel
Air
Reverb Furnace
Alloying Agent
Flux
Fuel
Rotary Furnace
Alloying Agent
Flux
Fuel
Crucible Furnace
Alloying Agent
Electricity
Flux
Electric Crucible Furnace
Alloy Ingots
Hardeners

Figure 9. Generalized flow diagram of a secondary brass and bronze recovery plant.[27]

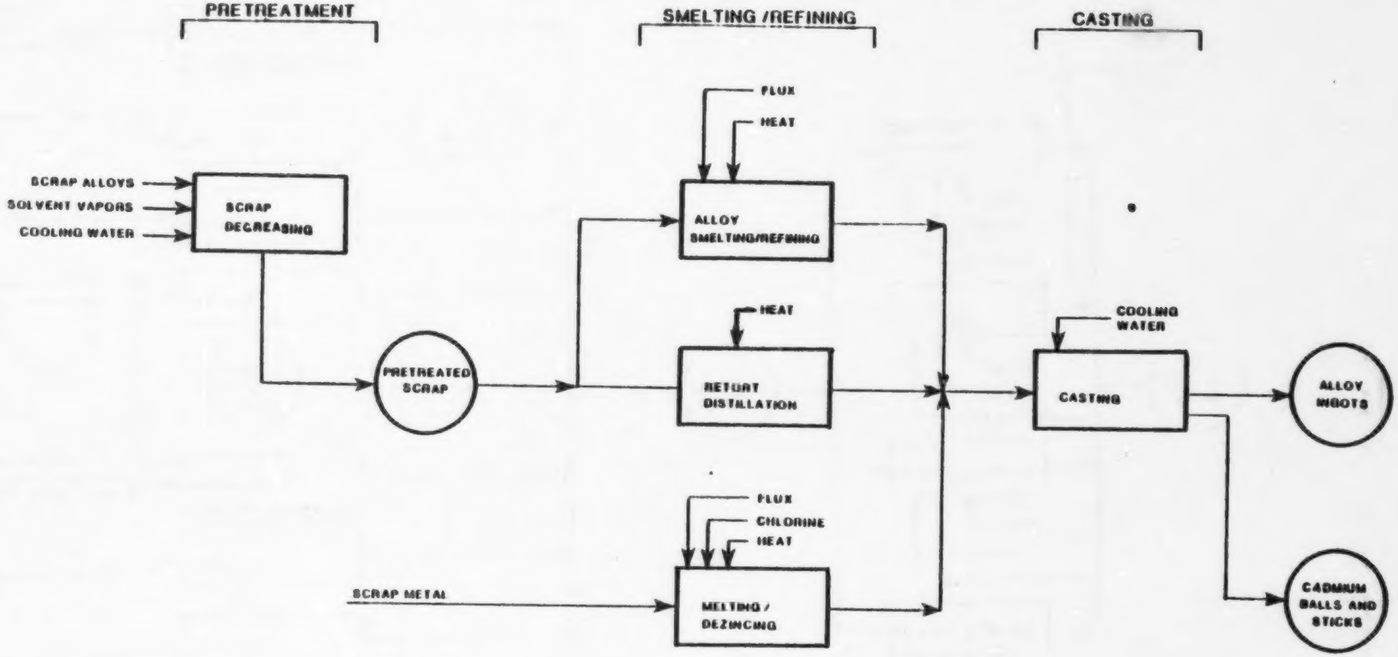

PRETREATMENT
SMELTING /REFINING
CASTING
SCRAP ALLOYS
SOLVENT VAPORS
COOLING WATER
SCRAP DEGREASING
PRETREATED SCRAP
FLUX
HEAT
ALLOY SMELTING/REFINING
HEAT
RETORT DISTILLATION
FLUX
CHLORINE
HEAT
SCRAP METAL
MELTING / DEZINCING
COOLING WATER
CASTING
ALLOY INGOTS
CADMIUM BALLS AND STICKS

Figure 10. Generalized flow diagram of a secondary cadmium recovery plant.[27]

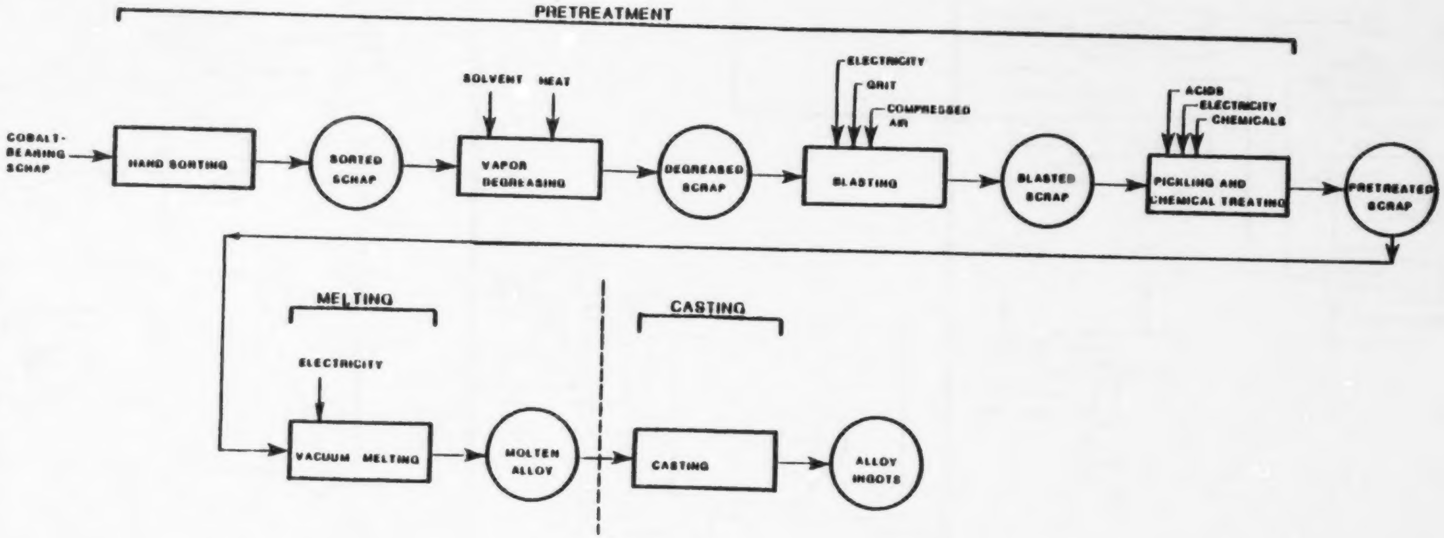

PRETREATMENT
COBALT-BEARING SCRAP
HAND SORTING
SORTED SCRAP
SOLVENT
HEAT
VAPOR DEGREASING
DEGREASED SCRAP
ELECTRICITY
GRIT
COMPRESSED AIR
BLASTING
BLASTED SCRAP
ACIDS
ELECTRICITY
CHEMICALS
PICKLING AND CHEMICAL TREATING
PRETREATED SCRAP
MELTING
ELECTRICITY
VACUUM MELTING
MOLTEN ALLOY
CASTING
CASTING
ALLOY INGOTS

Figure 11. Generalized flow diagram of a secondary cobalt recovery plant.[27]

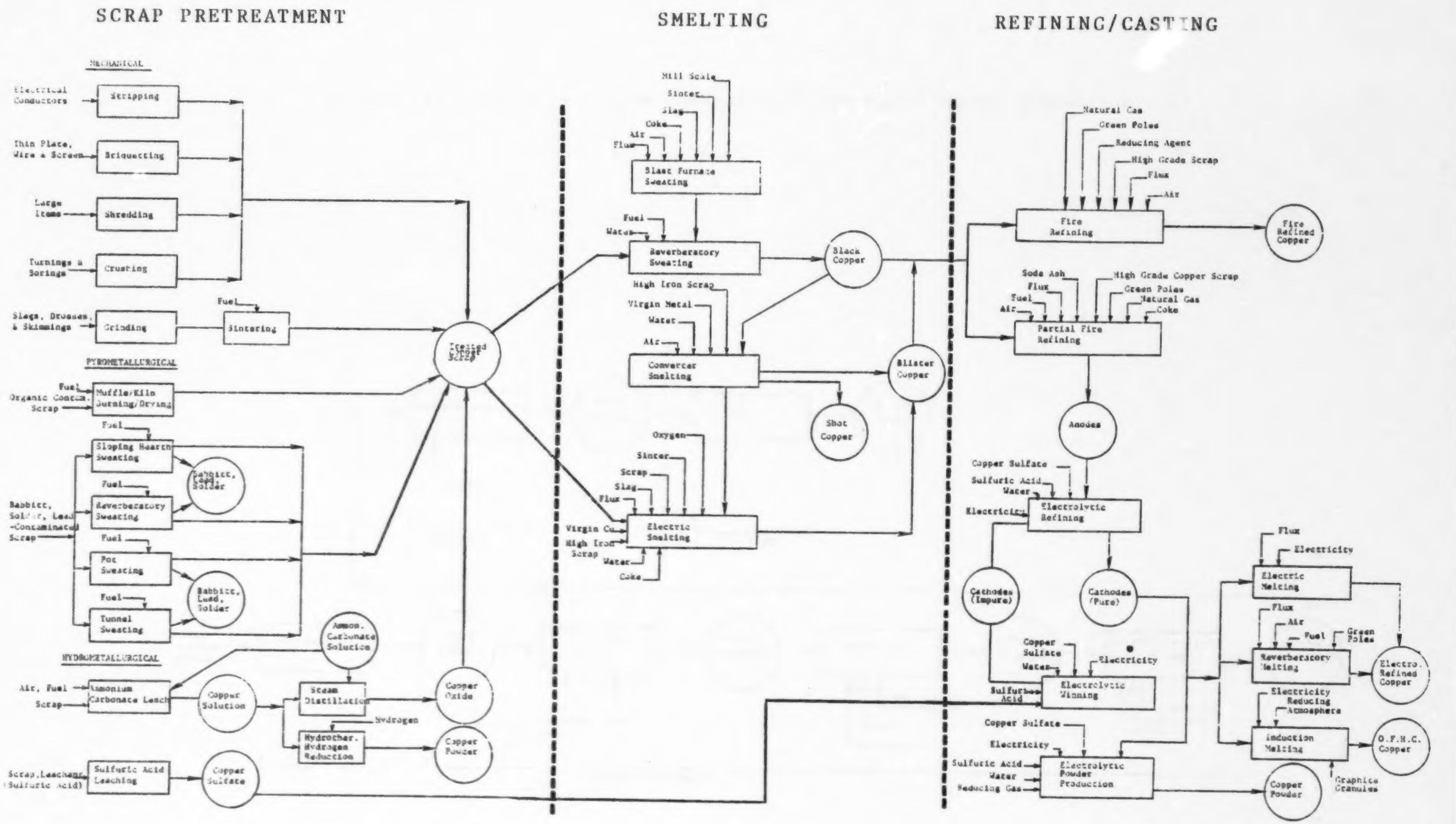

SCRAP PRETREATMENT
SMELTING
REFINING/CASTING
MECHANICAL
Electrical Conductors
Stripping
Thin Plate, Wire & Screen
Briquetting
Large Items
Shredding
Turnings & Borings
Crushing
Slags, Drosses, & Skimmings
Grinding
Fuel
Sintering
Treated Copper Scrap
PYROMETALLURGICAL
Fuel
Organic Contam. Scrap
Muffle/Kiln Burning/Drying
Fuel
Sloping Hearth Sweating
Fuel
Reverberatory Sweating
Babbitt, Solder, Lead -Contaminated Scrap
Fuel
Pot Sweating
Fuel
Tunnel Sweating
Babbitt, Lead, Solder
Babbitt, Lead, Solder
HYDROMETALLURGICAL
Air, Fuel
Scrap
Ammonium Carbonate Leach
Ammon. Carbonate Solution
Copper Solution
Steam Distillation
Hydrogen
Hydrother. Hydrogen Reduction
Copper Oxide
Copper Powder
Scrap, Leachant (Sulfuric Acid)
Sulfuric Acid Leaching
Copper Sulfate
Mill Scale
Sinter
Slag
Coke
Air
Flux
Blast Furnace Sweating
Fuel
Water
Reverberatory Sweating
Black Copper
High Iron Scrap
Virgin Metal
Water
Air
Converter Smelting
Blister Copper
Shot Copper
Oxygen
Sinter
Scrap
Slag
Flux
Virgin Cu
High Iron Scrap
Water
Coke
Electric Smelting
Natural Gas
Green Poles
Reducing Agent
High Grade Scrap
Flux
Air
Fire Refining
Fire Refined Copper
Soda Ash
Flux
Fuel
Air
High Grade Copper Scrap
Green Poles
Natural Gas
Coke
Partial Fire Refining
Anodes
Copper Sulfate
Sulfuric Acid
Water
Electricity
Electrolytic Refining
Cathodes (Impure)
Cathodes (Pure)
Copper Sulfate
Water
Electricity
Sulfuric Acid
Electrolytic Winning
Copper Sulfate
Electricity
Sulfuric Acid
Water
Reducing Gas
Electrolytic Powder Production
Copper Powder
Flux
Electricity
Electric Melting
Flux
Air
Fuel
Green Poles
Reverberatory Melting
Electro. Refined Copper
Electricity
Reducing Atmosphere
Induction Melting
O.F.H.C. Copper
Graphite Granules

Figure 12. Generalized flow diagram of a secondary copper recovery plant.[27]

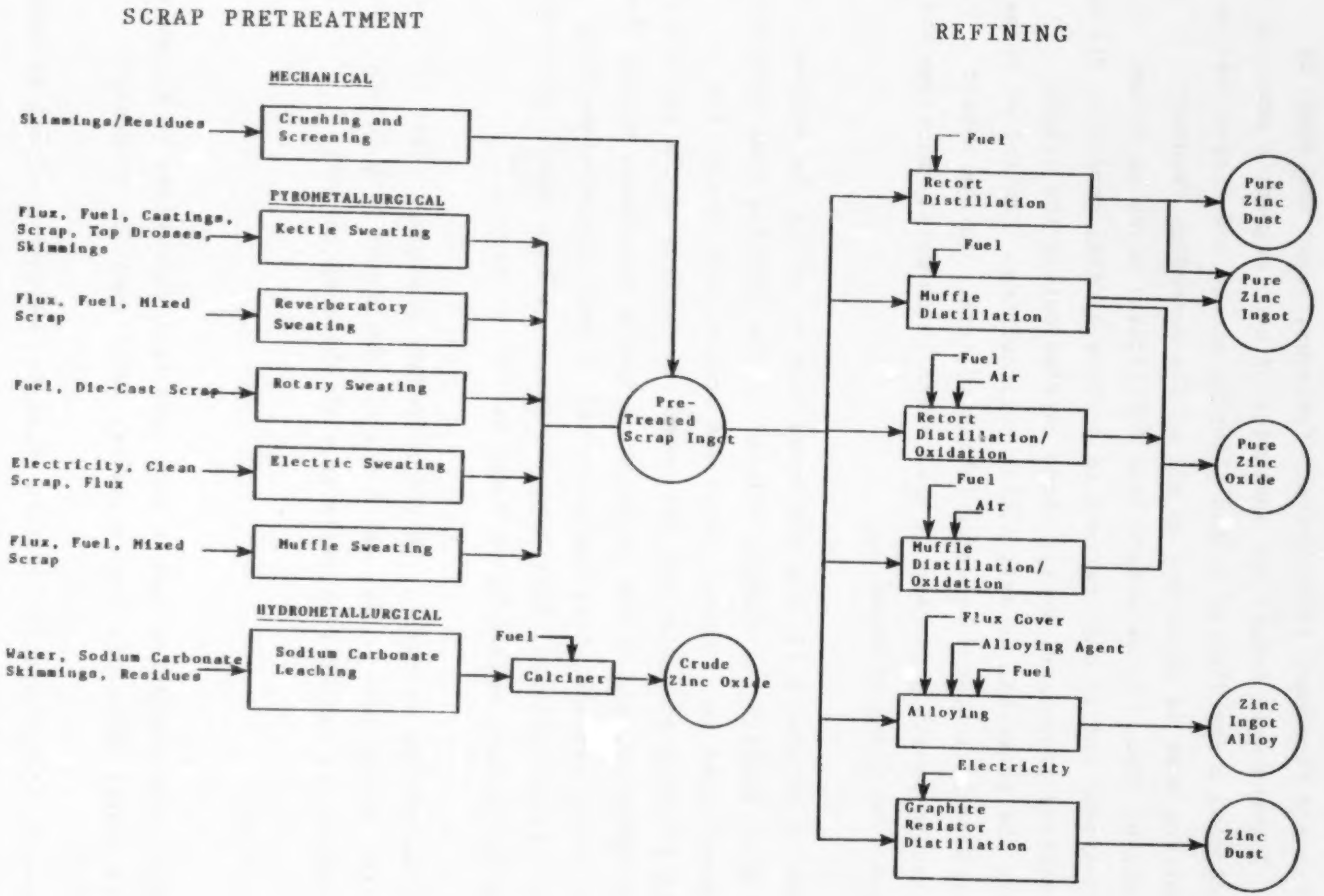

SCRAP PRETREATMENT
REFINING
MECHANICAL
Skimmings/Residues
Crushing and Screening
PYROMETALLURGICAL
Flux, Fuel, Castings, Scrap, Top Drosses, Skimmings
Kettle Sweating
Flux, Fuel, Mixed Scrap
Reverberatory Sweating
Fuel, Die-Cast Scrap
Rotary Sweating
Electricity, Clean Scrap, Flux
Electric Sweating
Flux, Fuel, Mixed Scrap
Muffle Sweating
HYDROMETALLURGICAL
Water, Sodium Carbonate Skimmings, Residues
Sodium Carbonate Leaching
Fuel
Calciner
Crude Zinc Oxide
Pre-Treated Scrap Ingot
Fuel
Retort Distillation
Fuel
Muffle Distillation
Fuel
Air
Retort Distillation/ Oxidation
Fuel
Air
Muffle Distillation/ Oxidation
Flux Cover
Alloying Agent
Fuel
Alloying
Electricity
Graphite Resistor Distillation
Pure Zinc Dust
Pure Zinc Ingot
Pure Zinc Oxide
Zinc Ingot Alloy
Zinc Dust

Figure 13. Generalized flow diagram of a secondary zinc recovery plant.[27]

The smelting step in secondary recovery facilities is performed by using electric arc furnaces, reverberatory furnaces, blast furnaces, or converters. Figures 8-13 detail the specifics of each segment's smelting process, including a description of the alloying agents and fluxes used in each. A smelting step is performed in all of the secondary recovery operations except zinc. In secondary zinc facilities, scrap is melted during pretreatment and is only refined to produce a final product. All of the other smelting processes, except those carried out in the cobalt segment, have the potential to emit nickel particulates. Control of these sources is generally achieved by using fabric filters. In the cobalt segment, a vacuum smelting process is used which traps metal emissions and prevents them from being released.[27]

As shown in Figures 8-13, the processes used to refine the various metals are often similar and closely related to the smelting step processes. In some segments such as aluminum, brass and bronze, and cobalt, the smelting and refining processes are the same. Regardless of the particular process configuration, all of the secondary refining processes, except those used in the cobalt segment, have the potential to emit nickel-containing particulate. Fabric filters, ESPs, and wet scrubbers have been applied to control the particulate emissions of these various processes.[27]

The metal casting operations in the secondary smelting plants involve pouring molten alloys into molds, which are air cooled to form ingots. No nickel emissions are generally associated with these operations.[27]

Emission Factors

No quantitative emission factor data have been determined to estimate the level of nickel emissions from secondary metal smelting processes.

No measured nickel speciation data exist for secondary nickel recovery plants; however, the forms of nickel potentially emitted from these facilities can be theorized from speciation results of other nickel metallurgical operations and a knowledge of the conditions existing within the recovery processes. Because of the high temperatures involved in the smelting and refining furnaces, the majority of nickel present should be oxidized. Data taken from a nickel alloy metallurgical plant indicate that nickel would exist predominantly as oxides of nickel and other metals and not pure nickel oxide although some is possible.[15] Some metallic nickel may also be present in the emissions from reasons connected with reaction kinetics. Data from the nickel alloy plant tests confirm that some metallic nickel is possible from a high temperature metallurgical environment involving nickel.[15]

Source Locations

The locations of firms which practice secondary recovery of metals, including aluminum, copper, zinc, cobalt, cadmium, and brass and bronze, are given in Table 5 of Section 3. These firms have been identified as having the potential to emit nickel compounds.

Co-Product Nickel Recovery

Process Description

As discussed in Section 3, nickel, in the form of nickel sulfate, is produced in varying quantities as a co-product of electrolytic copper and platinum metals refining plants. A representative electrolytic copper refinery flow diagram is presented in Figure 14 to illustrate how nickel sulfate is generated.[28] As shown in Figure 14, impurities in smelter-generated blister copper are separated from the copper product by electrolytic dissolution at an anode. Usually the electrolyte used is a solution consisting of copper sulfate and sulfuric acid. The electrolyte serves to dissolve the impurities in the copper anode. Those impurities not dissolved fall to the bottom of the electrolytic cell as a slime. In the electrolytic cell a portion of the dissolved copper is generally not transferred to the cathode. Therefore, a gradual increase occurs in the copper

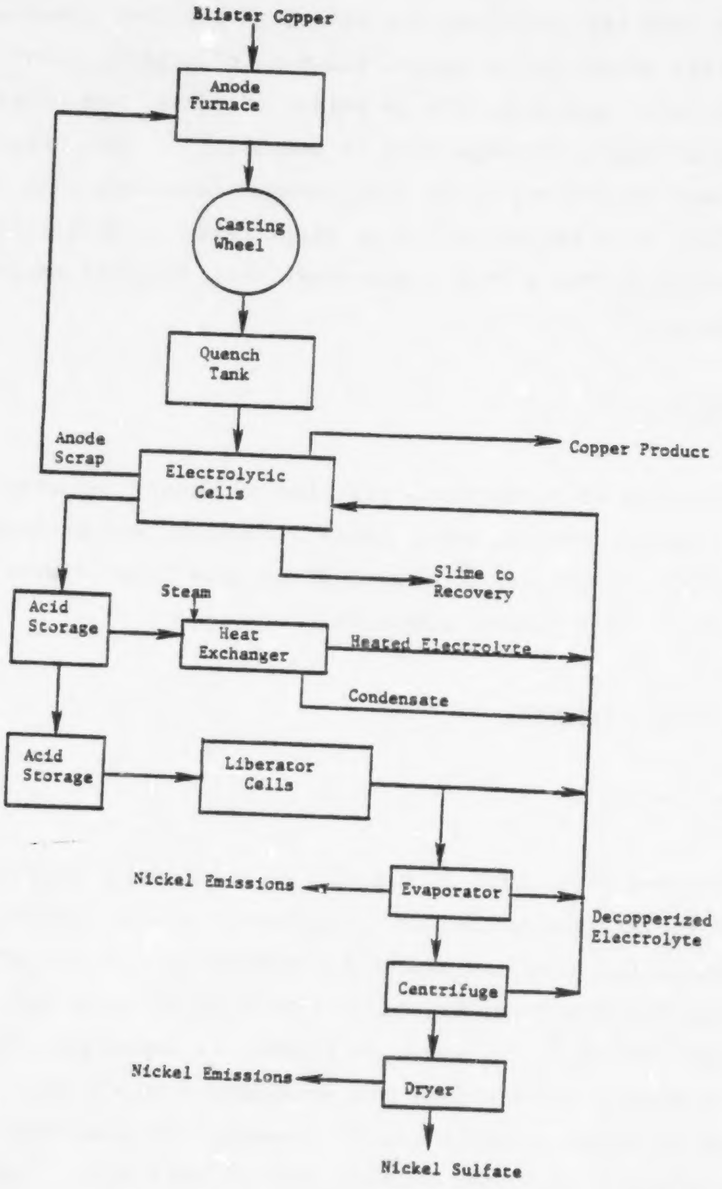

Blister Copper
Anode Furnace
Casting Wheel
Quench Tank
Anode Scrap
Electrolytic Cells
Copper Product
Slime to Recovery
Steam
Acid Storage
Heat Exchanger
Heated Electrolyte
Condensate
Acid Storage
Liberator Cells
Nickel Emissions
Evaporator
Decopperized Electrolyte
Centrifuge
Nickel Emissions
Dryer
Nickel Sulfate

Figure 14. Generalized flow diagram of an electrolytic copper refinery.[28]

concentration of the electrolyte. The concentration of copper and impurities in the electrolyte is controlled by continuously or intermittently withdrawing a portion of the used electrolyte and replacing it with a new solution.[28]

Copper is recovered from the electrolyte solution at the liberator cells. These liberator cells are similar to the electrolytic refining cells; however, insoluble iron or lead anodes are used in place of copper anodes. After the copper has been recovered in the liberator cells, the remaining solution is transferred to an open or vacuum evaporator and then to a centrifuge for the concentration and recovery of nickel sulfate. Nickel sulfate recovered from the centrifuge is dried and sold as a product, or is redissolved and recrystallized to produce a higher purity product.[28]

Emission Factors

Nickel emissions from electrolytic copper and platinum refining primarily occur from the evaporation and nickel sulfate drying operations. The evaporation operation produces nickel-containing aerosols, while the drying operation produces nickel sulfate particulate matter. Emissions are estimated to be low because (1) relatively few refiners practice nickel sulfate recovery, and (2) the most widely used evaporator systems are enclosed so that any emitted nickel aerosol is captured and recycled to the process.[29] No other quantitative data are available on nickel emissions from these processes.[28]

Ferrous and Nonferrous Metals Production

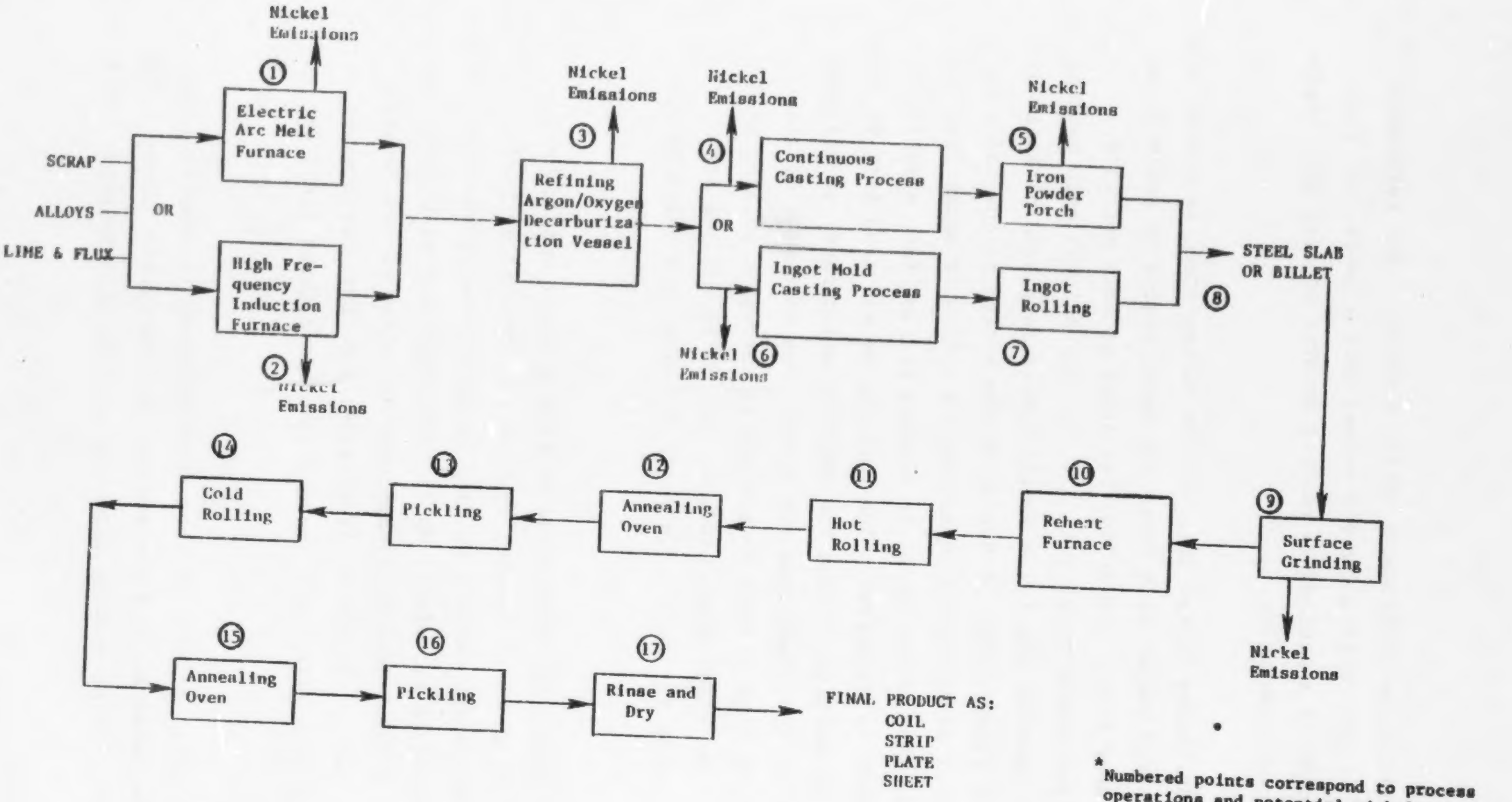
As discussed in Section 3, metallurgical uses constitute the largest demand for nickel. Nickel is used to produce two main categories of metal alloys: ferrous and nonferrous. Important ferrous nickel alloys include cast irons (which are produced in foundries), stainless steels, and alloy steels. Nonferrous nickel alloys include nickel-copper alloys, copper-nickel alloys, superalloys, and electrical alloys. Although individual plant configurations and techniques may vary between manufacturers, the basic processes used to produce either the ferrous or nonferrous materials are the same. In the following paragraphs process descriptions are presented that are representative of ferrous and nonferrous nickel metal production facilities. A discussion of the level of nickel emissions from each metals category and the location of ferrous and nonferrous facilities is presented after each process description.

Ferrous Metals Production

Process Description

The general flow process for the production of a nickel stainless steel or steel alloy is depicted in Figure 15. As shown in the figure, the process is initiated by charging scrap metal (similar in composition to the metal being produced), alloying materials, and a lime fluxing agent to either an electric arc or high frequency induction furnace for melting (pts. 1 or 2). The majority of steels produced are melted by electric arc furnaces. The types and quantities of alloying materials added are dependent upon the type of steel to be produced. Ferronickel, ferrochromium, pure unwrought nickel, nickel oxide, ferrosilicon, ferromanganese, and manganese silicon are examples of typical alloying materials.

After the furnace charge has been melted, the molten steel is mechanically transferred from the furnace by a ladle to the argon oxygen decarburization (AOD) process (pt. 3). The AOD process is a step to refine the molten steel. In 1978 over 80 percent of all domestically produced stainless steel was refined by the AOD process. Other, less frequently used refining techniques include vacuum arc remelting, electroslag remelting, and vacuum decarburization. In the AOD process, controlled amounts of oxygen and argon, and in some cases nitrogen, are blown through the bottom of the AOD vessel to remove excess carbon. During the AOD operation, the


SCRAP
ALLOYS
LIME & FLUX
OR
①
Electric Arc Melt Furnace
Nickel Emissions
②
High Frequency Induction Furnace
Nickel Emissions
③
Refining Argon/Oxygen Decarburization Vessel
Nickel Emissions
④
Nickel Emissions
OR
Continuous Casting Process
Ingot Mold Casting Process
⑥
Nickel Emissions
⑤
Iron Powder Torch
Nickel Emissions
⑦
Ingot Rolling
⑧
STEEL SLAB OR BILLET
⑨
Surface Grinding
Nickel Emissions
⑩
Reheat Furnace
⑪
Hot Rolling
⑫
Annealing Oven
⑬
Pickling
⑭
Cold Rolling
⑮
Annealing Oven
⑯
Pickling
⑰
Rinse and Dry
FINAL PRODUCT AS:
COIL
STRIP
PLATE
SHEET

*Numbered points correspond to process operations and potential nickel emission streams as discussed in the text.

Figure 15. Representative process flow diagram of a ferrous metal production facility.[30]

temperature of the molten metal is about 1565°C (2850°F). The refined, extremely hot metal is poured from the AOD vessel into a ladle. At that point it is either cast in a continuous casting machine or cast into ingots using conventional cast iron molds.

In a typical continuous caster (pt. 4), the molten steel is poured into a vertical, water cooled copper mold where the metal begins to solidify and emerges as a continuous slab. The solidified steel is then cut into sections using an iron powder torch (pt. 5). In conventional mold pouring operations known as teeming (pt. 6), a special ladle is placed directly over the open tops of the ingot molds. A nozzle on the bottom of the ladle is connected to a stopper mechanism which controls the flow of metal from the ladle into the mold. The molten steel is allowed to flow into a series of molds until the supply is exhausted. The ingot molds are then left to cool, allowing the steel to solidify. Once the ingot is solidified, an overhead crane is used to strip the steel from the molds. The thickness of the semi-finished steel is then reduced by running it through a rolling mill operation (pt. 7). The steel slabs produced (pt. 8) by rolling are generally about 15 cm (6 in) thick, 0.61 m (2 ft) wide, and 2.4 m (8 ft) long.[30]

Slabs made by either the continuous casting or ingot method have surface blemishes and an oxide coating that must be removed by surface grinding (pt. 9) before any further rolling or metal forming can take place. Ingot slabs are ground on all sides, while continuous-cast slabs are usually ground on only two sides. Because continuous-cast slabs do not require initial rolling to reduce thickness, fewer surface defects are present on the slab sides, and less grinding is needed to prepare these slabs for further processing.

To resume the metal forming process after grinding is complete, the steel slabs must be reheated to a temperature of 1200-1260°C (2200-2300°F). Reheat furnaces (pt. 10) or soaking pits are used for this purpose. Once the slab is malleable, it passes through a series of reduction and finishing mills (pts. 11, 14) of widely varying design among manufacturers. The final required product determines the number of mills used.

Two important processes that are conducted during the reduction and finishing operation are annealing and pickling. Hot rolling of stainless steel to a desired thickness produces distortion in the metal grain structure and builds up internal stresses in the metal. The high temperature annealing operation (pts. 12, 15) recrystallizes the grain structure, relieves the internal stresses, and dissolves any chromium carbides present. It also produces an oxide film on the surface of the metal known as scale. Scale is removed by pickling (pts. 13, 16), which involves immersing the steel in specialized acid baths. The pickling baths may be either hot or cold operations. Following the final pickling operation the steel product is rinsed, dried, and removed to a storage area.

The production process described above (and shown in Figure 15) for stainless and alloy steels is generally applicable to basic iron and steel (carbon steel) plants except for differences in the types of melt furnaces used. Iron and steel plants employ basic oxygen, open hearth, or electric furnaces to melt the charge materials. High frequency induction furnaces are not used.

Emission Factors

In the production of nickel stainless and alloy steels and cast irons, the charge melting furnace (pts. 1, 2) is a major source of nickel-containing particulate emissions.[26,30] Tapping and material transfer operations at the furnace generate considerable fugitive particulate emissions which also contain nickel and nickel oxides. The steel industry generally controls furnace emissions by the use of collection hoods and standard particulate control devices such as fabric filters or ESPs. A second important source of nickel emissions is the AOD process vessel (pt. 3). As is the case with the melt furnaces, considerable nickel-containing, fugitive particulate emissions are released during tapping and material transfer operations from the AOD vessel. Hooding and induced draft roof designs are used to capture the particulate emissions. Fabric filters are successfully being used to control the collected emissions.[31,32]

A third major source of nickel emissions is the surface grinding operation (pt. 9). As the grinding wheel contacts the metal surface, particles are displaced and emitted. Different manufacturers use various hooding designs to capture the emitted particulates, which are then directed to a fabric filter or other particulate removal device for control.

Other less significant nickel emission sources include the casting operations (pts. 4,6) and the iron powder torch cutting operation (pt. 5). As molten metal is transferred to the continuous caster or the teeming ladle, fumes evolve that may contain nickel. Hooding and the induced draft roof system are used to remove the fumes from the work area. A similar situation exists with the torch cutting operation. As the slabs are cut, fumes are released which potentially contain nickel. Downdraft hoods, which are placed beneath the steel being cut, are used to remove these fumes from the work area.

Potential nickel emission points, including fugitive emission sources, are indicated in Figure 15. With the exception of the AOD operation, basic iron and steel plants contain the same potential nickel emission sources that have been described above for nickel stainless and alloy steel facilities.

Nickel emission factors for the steel industry have been estimated based on steel industry particulate emission factors and data on the nickel content of emitted particulates.[33-36] The calculated factors are presented in Table 13. Both the particulate emission factors and the nickel content data are based on the results of many source tests in the steel industry.

TABLE 13. NICKEL EMISSION FACTORS FOR STEEL MANUFACTURING OPERATIONS[33-36]

Source	Controls in Place[a]	Emission Factor, kg (lb) Ni per Mg (ton) of steel produced[b] kg/Mg	lb/ton
Open Hearth Furnace	ESP	0.00009	(0.00018)
Open Hearth Fugitive Emissions	None	0.000025	(0.00005)
Basic Oxygen Process Furnace	Scrubber	0.000009	(0.000018)
Basic Oxygen Process Fugitives	None	0.00005	(0.0001)
Electric Arc Furnace (Carbon Steel)	None	0.0042	(0.0083)
Electric Arc Furnace (Carbon Steel)	FF	0.000007-0.000042	(0.000013-0.000084)
Electric Arc Furnace (Alloy Steel)	None	0.013	(0.025)
Electric Arc Furnace (Alloy Steel)	FF	0.00002-0.00013	(0.000039-0.00025)
Electric Arc Furnace Fugitive Emissions (Carbon Steel)	None	0.00027	(0.00054)
Electric Arc Furnace Fugitive Emissions (Alloy Steel)	None	0.0008	(0.0016)
Electric Arc Furnace Fugitive Emissions (Carbon Steel)	Hoods & FF	0.00006	(0.00011)
Electric Arc Furnace Fugitive Emissions (Alloy Steel)	Hoods & FF	0.00016	(0.00032)
Electric Arc Furnace (Stainless Steel)	None	0.15	(0.3)
Electric Arc Furnace (Stainless Steel)	FF	0.0015	(0.003)
Electric Arc Furnace Fugitive Emissions (Stainless Steel)	None	0.018	(0.036)
Electric Arc Furnace Fugitive Emissions (Stainless Steel)	Hoods & FF	0.0036	(0.0072)
Argon Oxygen Decarburization Vessel (Stainless Steel)	None	0.16	(0.32)
Argon Oxygen Decarburization Vessel (Stainless Steel)	FF	0.032	(0.064)

[a] ESP = electrostatic precipitator
FF = fabric filter

[b] Emissions are expected to be in the form of complex oxides of nickel and other metals, nickel oxide, nickel sulfate, and metallic nickel. All factors are expressed in terms of total nickel.

Factors are only available for melting furnaces and furnace fugitive emissions. No emission factor data were available to characterize other steel sources such as grinding and casting processes.

One other set of emission factor data has been developed in a study by Purdue University for this source category.[37] In that study an open hearth furnace was tested for both controlled and uncontrolled nickel emissions. The average controlled nickel emissions from the ESP system controlling the melt furnace were 0.00055 kg/Mg (0.0011 lb/ton) of steel produced. The average emission factor for uncontrolled emissions from the furnace was 0.0042 kg/Mg (0.0085 lb/ton) of steel produced.[37]

In the high temperature metallurgical processes occurring in steelmaking furnaces, the majority of nickel present would be expected to be oxidized. Data from the steelmaking industry and from the related nickel alloy industry confirm that the majority of nickel present in emissions from metallurgical melting furnaces is in the form of complex oxides of nickel and other metals.[15,38] In one test of nickel emissions from an EAF producing stainless steel, only 5 percent of the total nickel present was water soluble.[38] The nickel in the insoluble phase was determined to exist as an alloyed element in iron oxide particles. In the same series of tests nickel emissions from surface grinding of stainless steel were determined to exist as metallic nickel, while emissions from manual metal arc and metal inert-gas welding of stainless steel contained nickel as nickel oxide.[38]

Tests of the emissions from an EAF producing carbon steel identified nickel oxide to constitute from 0 to 3 percent of total particulate emissions. Similar work on the emissions from an AOD vessel handling specialty steel produced one sample where nickel oxide constituted 3.1 percent of total particulate emissions.[35,39-42]

Data taken from tests of EAF's in a high-nickel alloy plant support the observations made from the steelmaking industry tests. Dust samples taken in these tests were analyzed primarily by X-ray diffraction and also some selected samples were analyzed by energy dispersive X-ray analysis. All samples were viewed under a scanning electron microscope. Nickel in particulate emissions from melting furnaces was found to exist mainly as oxides of nickel and other metals (primarily iron) followed by lesser amounts of metallic nickel and nickel oxide.[15,43]

Although these results cannot be extrapolated directly to nickel emissions from steel manufacturing, the indications are clear that nickel in high temperature metallurgical environments is predominantly oxidized and combined with other metals present (if stoichiometry permits) to form complex oxides of nickel and other metals. From available data it is difficult to predict the extent to which metallic nickel would be found in steelmaking particulate emissions. However, because metallic nickel is unstable relative to nickel oxide over a wide temperature range, any non-oxidation of the metallic nickel present is probably due to a specific feature of the overall steelmaking process reaction kinetics.[15]

The only sulfur compound of nickel expected to be emitted from steelmaking processes is nickel sulfate. Generally, in these metallurgical operations attempts are made to exclude sulfur from the reactions; however, small amounts can be present. If sulfur is present (usually as sulfur dioxide), sulfate and consequently nickel sulfate can and would be formed over nickel sulfide or nickel subsulfide because it is thermodynamically more stable under these types of temperature conditions than either of the sulfide compounds. Essentially the reactions shown below would not occur because sulfur pressures present would not be sufficient to bring about the reaction.

$$(1)\quad 3Ni(s) + 2SO_2(g) \rightarrow Ni_3S_2(s) + 2O_2(s)$$

$$(2)\quad Ni(s) + SO_2(g) \rightarrow NiS(s) + O_2(g)$$

Sulfate and chloride anions have been identified in the small water soluble portion of steelmaking dusts such that it is likely that a minor part of the emissions generated from steelmaking contain nickel sulfate and nickel chloride.[15,43]

Source Locations

Because of the large number of plants involved in this category of nickel emission sources, it is not feasible to present an individual plant listing. However, the national distribution of nickel emissions from ferrous metals production is shown in Table 14.[44] Directories such as The Thomas Register, Dunn and Bradstreet, or Standard and Poor's could be used to identify individual site locations. The necessary SIC codes to access published directories are given below:

- SIC 331, Blast Furnaces, Steel Works, and Rolling and Finishing Mills
- SIC 332, Iron and Steel Foundries

In addition, the following trade associations should have listings of domestic ferrous metals production facilities from a compilation of their membership.

- American Iron and Steel Institute (Directory of Iron and Steel Works of the United States and Canada)
- The Ferroalloys Association
- American Foundrymen's Society
- Cast Metals Federation

A partial list of firms identified under the ferrous metals category is given in Table 15.

TABLE 14. DISTRIBUTION OF NICKEL EMISSIONS FROM FERROUS METALS PRODUCTION BY GEOGRAPHIC REGION[44]

Geographic Region	Percentage of Nickel Emissions From Ferrous Metals Production
New England	0.48%
Middle Atlantic	22.8%
East North Central	26%
West North Central	2.4%
South Atlantic	13.2%
East South Central	20%
West South Central	2.5%
Mountain	5.8%
Pacific	6.9%

TABLE 15. PARTIAL LIST OF DOMESTIC FIRMS PRODUCING NICKEL-CONTAINING FERROUS METALS[30]

Stainless Steel Melting Firms	Alloy Steel Melting Firms
Allegheny Ludlum	Bethlehem Steel Corporation
Al-Tech Specialty	Braeburn Alloy Steel
Armco[a]	Columbia Tool Steel Company
Babcock and Wilcox	Teledyne Vasco
Carpenter Technology	
Crucible Steel	
Cyclops Corporation[a]	
Eastern Stainless	
Electroalloy Corporation	
Ingersoll	
Jessop Steel[a]	
Jones and Laughlin[a]	
Jorgenson	
Josyln Stainless	
McLouth Steel[a]	
National Forge	
Republic[a]	
Simonds Steel	
Timken	
U. S. Steel[a]	
Washington Steel Corporation	

[a] Also produces carbon steel.

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of nickel emissions from any given facility if a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

This is considered a partial list because the reference cited does not necessarily contain the name of each company making nickel-containing steel. Because of the size and diversity of this industry, it is possible that more companies are involved than are given here.

Nonferrous Metals Production

Process Description

Many nickel alloys are produced in this category, including copper-nickel, nickel-copper, electrical, super, and permanent magnet alloys. Each alloy is designed and manufactured to have a composition that facilitates its final end use in an environment that is generally corrosive, stressful, or hot. Table 16 presents a list of the more prominent nickel alloys and their chemical composition.[45]

Nonferrous nickel alloys are produced in the form of rods, sheets, and tubes. These semifinished materials are then used to fabricate finished products. The production of all nickel alloys starts with a common process step in which melting (and in some cases refining) of the input materials is performed. From this point the processing differs depending on the type of alloy produced. Further processing steps include casting, hot and cold working, and powder production.

A generalized flow diagram is given in Figure 16 depicting the possible methods of nickel alloy production. Initially, the charge materials consisting of pure nickel pellets, alloy scrap, and other alloying agents are added to the melt furnace. Primary melting of the charge materials is accomplished by using one of several types of furnaces including an electric arc, vacuum induction, vacuum arc, or electron beam furnace (pt. 1, Figure 16).[46] Electric arc furnaces are prevalent in this industry; however, vacuum induction furnaces are used in melting alloys with highly oxidizable metals, and electron beam furnaces are used for alloys containing highly refractory metals.

As the melting process in an electric arc furnace is carried out, slag tapping is accomplished through a tap spout on one side of the furnace. Slag is poured into a slag pot and transported to a cooling area where it

TABLE 16. MAJOR NICKEL ALLOYS AND THEIR CHEMICAL COMPOSITION 45

Alloy[a]	Chemical Composition, wt. percent										
	Ni	Fe	Cr	Cu	Mo	Mn	Si	C	Al	Ti	Other
Nickel 200	99.5	0.15		0.05		0.25	0.05	0.06			
Monel Alloy 400	66.5	1.25		31.5		1.0	0.25	0.15			
Monel Alloy K-500	65.0	1.0		29.5		0.6	0.15	0.15	2.8	0.5	
Nichrome	77.0	0.5	20.0			1.0	1.0	0.06			
Inconel Alloy 600	76.0	8.0	15.5			0.5	0.2	0.08			
Hastelloy Alloy B-2	65.4	2.0	1.0		28.0	1.0	0.1	0.02			2.5 Co
Hastelloy Alloy G	42.0	19.5	22.0	2.0	6.5	1.5	1.0	0.05			2.5 Co, 2.0 (Cb+Ta), 1.0 W
Hastelloy Alloy C-276	55.4	5.0	16.0		16.0	1.0	0.08	0.02			2.5 Co, 4.0 W
Inconel Alloy 718	52.5	18.5	19.0		3.0	0.2	0.2	0.04	0.5	0.9	5.1 Cb
B-1900	64.0		8.0		6.0			0.1	6.0	1.0	10.0 Co, 4.0 Ta, 0.015 B, 0.1 Zr
Mar-M200	60.0		9.0					0.15	5.0	2.0	10.0 Co, 12.0 W, 1.0 Cb, 0.015 B, 0.05 Zr
Waspaloy	58.0		19.5		4.3			0.08	1.3	3.0	13.5 Co, 0.006 B, 0.06 Zr
Udimet 500	54.0		18.0		4.0			0.08	2.9	2.9	18.5 Co, 0.006 B, 0.05 Zr
Udimet 700	53.0		15.0		5.2			0.08	4.3	3.5	18.5 Co, 0.03 B
Nimonic Alloy 80A	76.0		19.5			0.3	0.3	0.06	1.4	2.4	0.003 B, 0.06 Zr
Nimonic Alloy 115	60.0		14.3		3.3			0.15	4.9	3.7	13.2 Co, 0.16 B, 0.04 Zr
Rene' 41	55.0		19.0		10.0			0.09	1.5	3.1	11.0 Co, 0.005 B
Inconel Alloy 754	78.0		20.0					0.05	0.3	0.5	0.6 Y_2O_3

[a] Monel, Duranickel, Inconel, Incoloy and Nimonic are trademarks of INCO companies; Hastelloy is a trademark of the Cabot Corporation; Udimet is a trademark of the Special Metals Corporation, Mar M is a trademark of the Martin Marietta Corporation; Rene 41 is a trademark of Teledyne Allvac; and Waspaloy is a trademark of United Technologies Corporation.

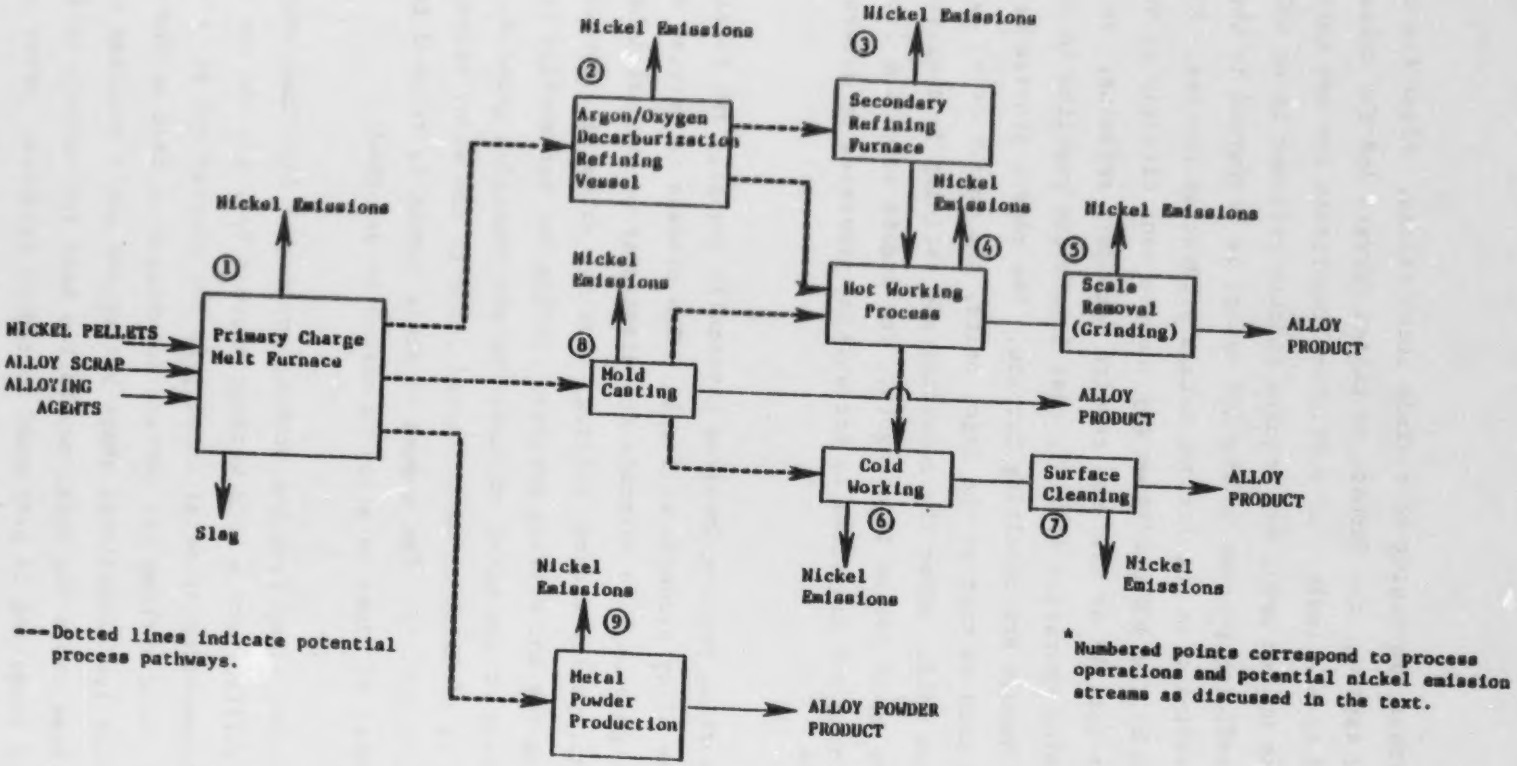

Nickel Emissions
Nickel Emissions
Nickel Emissions
①
②
③
Argon/Oxygen Decarburization Refining Vessel
Secondary Refining Furnace
Nickel Emissions
④
Nickel Emissions
⑤
NICKEL PELLETS
ALLOY SCRAP
ALLOYING AGENTS
Primary Charge Melt Furnace
Nickel Emissions
⑧
Mold Casting
Hot Working Process
Scale Removal (Grinding)
ALLOY PRODUCT
ALLOY PRODUCT
Cold Working
Surface Cleaning
ALLOY PRODUCT
⑥
⑦
Slag
Nickel Emissions
⑨
Nickel Emissions
Nickel Emissions
Metal Powder Production
ALLOY POWDER PRODUCT
---Dotted lines indicate potential process pathways.
*Numbered points correspond to process operations and potential nickel emission streams as discussed in the text.

Figure 16. Representative process flow diagram of a nonferrous metal, nickel alloy production facility.46

may undergo further processing to reclaim metal values. After the completion of slag tapping, the furnace is tilted forward and the melted metal alloy is poured into a ladle. If sufficient impurities are not carried out in the slag, the molten metal may require further refining in an AOD unit (pt. 2). The refining process in the AOD vessel is performed in the same manner as AOD refining in the ferrous metals production process. Alloy ingots produced by the AOD operation may then be sent directly to the hot working process (pt. 4) or they may require secondary refining. In the secondary refining operation (pt. 3), cast ingots are remelted in either an electroslag or vacuum arc remelting furnace. The remelt process is conducted in a mold so that as the ingot melts, the molten metal is contained in the mold. After the remelting and refining is complete, the molten metal is again poured into ingots. The ingots resulting from secondary refining are subjected to hot working processes to determine their product form.[46]

The hot working process involves physically changing and forming the shapes that the alloy products will take. The process is carried out at temperatures high enough to maintain the plasticity of the metal being formed. The alloys may undergo rolling, drawing, extruding, forging, and pressing during the hot working process. During the hot working process, scale may develop on the metal surface, thereby requiring grinding, sandblasting, or pickling to be performed prior to the alloy becoming a finished product (pt. 5). The amount of scale formed is related to the degree and number of times an alloy is shaped or deformed.

As the nickel alloy from hot working approaches its final shape, the alloy may be shifted into a cold working process (pt. 6). As the name implies, this operation of metal forming is not carried out at elevated temperatures. Cold working has certain advantages in that as the metal is worked, it holds its dimensional shape better and scale problems are avoided. In some cases the metal may be too hard for certain cold working operations and annealing is performed to reduce hardness. After annealing, pickling may be needed to clean the metal surface (pt. 7).

If the molten alloy from the primary melt furnace does not require further refining, it may be sent directly to casting (pt. 8) or to the metal powder production process (pt. 9). Casting essentially consists of pouring molten metal into a mold to form a useful shape. The molten metal in the mold is generally allowed to air cool. If necessary, the cooled product from casting may undergo further forming or shaping in either the hot or cold working processes.

For alloys that, because of their particular physical properties, are very hard to work, powder metallurgy is often employed to produce the required alloy shapes. Powder metallurgy (pt. 9) involves atomizing the molten metal from the primary melt furnace to form spherical metal droplets. The most frequently used atomization method is the inert gas atomization method, with argon as the usual inert gas. Nickel alloy droplets are formed by impacting the molten metal with a high velocity argon stream. Alloy powders formed in this way can more easily be compressed to form the required shapes and products.

Emission Factors

The primary nickel emission sources within a nickel alloy facility are the melting furnaces (pts. 1, 3), the casting process (pt. 8), the hot and cold working processes, the powder production process (pt. 9), and the scale removal (surface grinding) process (pt. 5).[46] These various emission points are indicated in Figure 16. The emissions from these points are in the form of dust and fumes.[19,26,47] The method generally employed throughout the industry for the control of the alloy-generated nickel emissions involves collecting them by the use of various hooding designs and directing the collected particles to a fabric filter system. Fabric filters in this application have estimated control efficiencies in excess of 99 percent.[46] Most important, however, in an alloy facility's overall nickel control system is the ability of the hooding system to collect emissions efficiently. Sidedraft, canopy, and full roof hooding designs have been shown to be effective in this industry. Table 17 presents a description of the controls used at one nickel alloy facility that is considered to be representative of the industry.[46]

In Table 18, nickel emission factors are presented for several types of nickel alloy facilities. The emission factors presented apply only to a facility's individual melt furnaces. No emission factor data were available to characterize other sources such as the AOD vessel, powder production, hot and cold working processes, and casting processes.

Very few specific data were found which identified the species or form of nickel in emissions generated during alloy production. The International Nickel Company (INCO) has, however, performed several analyses of dusts collected during the manufacture of high nickel alloys using X-ray diffraction, scanning electron microscopy (SEM), and energy dispersive X-ray analysis.[15] Particles collected during the melting of Monel® 400 and K-500 alloys which contain about 66.5 percent nickel, 1 percent iron, and 30 percent copper, were spherical, which was considered typical of metal that has condensed from the vapor state. The X-ray diffraction pattern of the dust was compared to several patterns in a reference library; patterns for nickel oxide and a complex copper-nickel oxide closely matched that of the unknown dust. Of the particles examined using EDXA, none were found to be copper-free, therefore, the existence of nickel oxide as a separate species in the particles is doubtful.[15]

Using the same techniques, dusts collected during melting of Inconel 800 and 840 were thought to contain complex nickel-iron oxides, nickel-chromium oxides, and nickel oxide. These alloys contain approximately 32 percent nickel, 46 percent iron, and 21 percent chromium. Similarly, dusts from melting Inconel 600 (76 percent nickel, 8 percent iron, 15.5 percent chromium) were thought to contain nickel oxide and a complex iron-nickel oxide. EDXA indicated the presence of substantial amounts of

TABLE 17. REPRESENTATIVE EMISSION CONTROL EQUIPMENT USED IN NICKEL ALLOY PRODUCTION[46]

Part of the Alloy Process Controlled	Control Equipment Configuration
Electric arc melt furnace and AOD vessel	- Water-cooled, side draft hoods on the furnaces - Canopy hood in building roof to collect particulate emissions during tapping operations - All hoods vent to a fabric filter system
Secondary refining in an induction furnace	- Traversing hood positioned over the furnace - Hood vents to a fabric filter
Surface grinding for scale removal	- Fixed hoods placed directly over grinders to collect fine particulate emissions - Hoods vent to a fabric filter

TABLE 18. NICKEL EMISSION FACTORS FOR NONFERROUS METALS PRODUCTION SOURCES

Facility Type	Emission Factors[a]
Nickel-Copper, Copper-Nickel	1 kg/Mg (2 lb/ton) of Ni charged[b]
Superalloys	1 kg/Mg (2 lb/ton) of Ni charged[b]
Permanent Magnet Alloys	1 kg/Mg (2 lb/ton) of Ni charged
Electrical Alloys	1 kg/Mg (2 lb/ton) of Ni charged
Other Nonferrous Alloys	1 kg/Mg (2 lb/ton) of Ni charged

[a] All factors are engineering estimates from Reference 26 and represent controlled emissions from fabric filters. Emissions are expected to be in the form of metallic nickel, complex oxides of nickel and other metals, nickel oxide, and nickel sulfate. The factors apply to individual melting furnaces at each type of facility.

[b] Reference 19 reports nickel emissions from a high nickel alloy manufacturing plant as less than 0.25 kg/Mg (0.5 lb/ton) of nickel charged. The types and levels of control are not specified.

copper in the particles analyzed. The copper was probably present as a contaminant and does not indicate the presence of nickel-copper oxides from an alloy containing little or no copper.

A specialized Br_2/alcohol leaching technique was used to substantiate the absence of alloy or metal in Monel® 405 dusts. This method dissolves the metal but leaves oxides relatively intact. It was found that 5-10 percent of the nickel was present as the metal.[15] Dusts from Inconel 600 and Incoloy 800 were found to contain 7.8 and 4.1 percent metallic nickel, respectively.

Grinding dust was also examined and determined to be coarser than melting dusts and similar in composition to the parent material. Oxides were present on particle surfaces, but the particles were primarily metallic.

Based on these analyses, nickel emitted during alloying is likely to be present as a complex oxide of nickel, iron, and other metals present in each particular alloy such as chromium. Smaller amounts of metallic nickel and possibly some nickel sulfate may also be emitted.

Source Locations

Specific locations of the numerous firms producing nickel alloys can be found in the Thomas Register, keying on specific nickel alloy names including Monel®, Inconel®, Hastelloy®, Nimonic®, and Udimet®. In published manufacturing directories indexed by SIC code, SIC 335 (Rolling, Drawing and Extruding of Nonferrous Metals) can be used to locate possible nickel alloy producers.

Electroplating

Process Description

Nickel is plated onto metal by several means to provide decoration, corrosion resistance, electrical conducting properties, and mechanical wearing properties. Nickel plating is performed using both electrolytic and nonelectrolytic processes. Electrolytic plating of nickel includes electroplating and electroforming processes. Nonelectrolytic, chemical coating processes used in the industry include displacement coating (simple immersion) and autocatalytic reduction (electroless plating). For categorization purposes, the broad term electroplating is used to refer to the collection of all these plating processes, even though electroplating is a distinct type of plating technique. Each electrolytic and nonelectrolytic technique is discussed in the following paragraphs.

Electrolytic nickel plating basically consists of electrically depositing a thin coating of nickel on an object for decoration or protection purposes. The material or surface to be plated is generally treated prior to plating. Pretreatment may include polishing or grinding, solvent degreasing, electrolytic cleaning, or acid dipping to remove alkaline residues. Between pretreatment steps the surface being plated is rinsed. Frequently during pretreatment, an undercoat of copper is applied to the plating surface to facilitate better nickel coverage.

Most electrolytic electroplating operations are conducted in an electroplating tank with a cathode and an anode immersed in electrolyte. Generally, the part to be plated functions as the cathode, and the anode is a bar or slab of nickel metal. The electrolyte solution contains ions of the metal to be deposited and other additives such as sulfuric or fluoboric acid. The function of the acids is to improve the electrical conductivity of the electrolyte bath. Nickel sulfate and nickel chloride are the primary nickel compounds used to prepare electrolyte solutions.

To accomplish the plating process, low voltage direct current is passed through the electrolyte bath. Electrolytic decomposition of water in the bath occurs, thereby releasing hydrogen gas at the cathode and oxygen at the anode. As these gases rise to the surface of the bath, a mist of electrolyte is formed and nickel metal is deposited on the part. During plating, the pH and temperature of a sulfamate bath are 3-4 and 40-68°C (104-154°F), respectively. The equivalent values for a fluoborate bath during plating are 2.7-3.5 and 35-65°C (95-149°F). Figure 17 illustrates the basic process steps that are found in a representative electroplating facility.[48-51]

A specialized application of the electrolytic electroplating process is known as electroforming. Electroforming is the production of an article by electro-deposition upon a mold that is subsequently separated from the deposited material. The mechanics of the electroforming process are essentially the same as the electroplating process previously described. The main difference between the two processes is that the electroforming process requires more time to accomplish the material deposition. To speed up the process, electroforming baths are operated at the highest possible electrical current density. The increased current density creates a greater potential for electrolyte misting than is found in standard electroplating.

The displacement or nickel immersion plating process is generally known as nickel dip plating. The process basically involves the replacement of the surface atoms of a solid base metal with nickel from solution. As the base metal dissolves, it provides electrons to reduce the nickel ions. A dilute solution of nickel sulfate with a pH of 3-4 and a temperature of 70°C (160°F) is used for the displacement bath. The only large-scale operation where this method of nickel plating is prominent is the coating of steel in the ceramic enameling industry.[19,48-51]

The process of autocatalytic reduction, or electroless plating, involves coating metallic parts with an ultra-micro crystalline

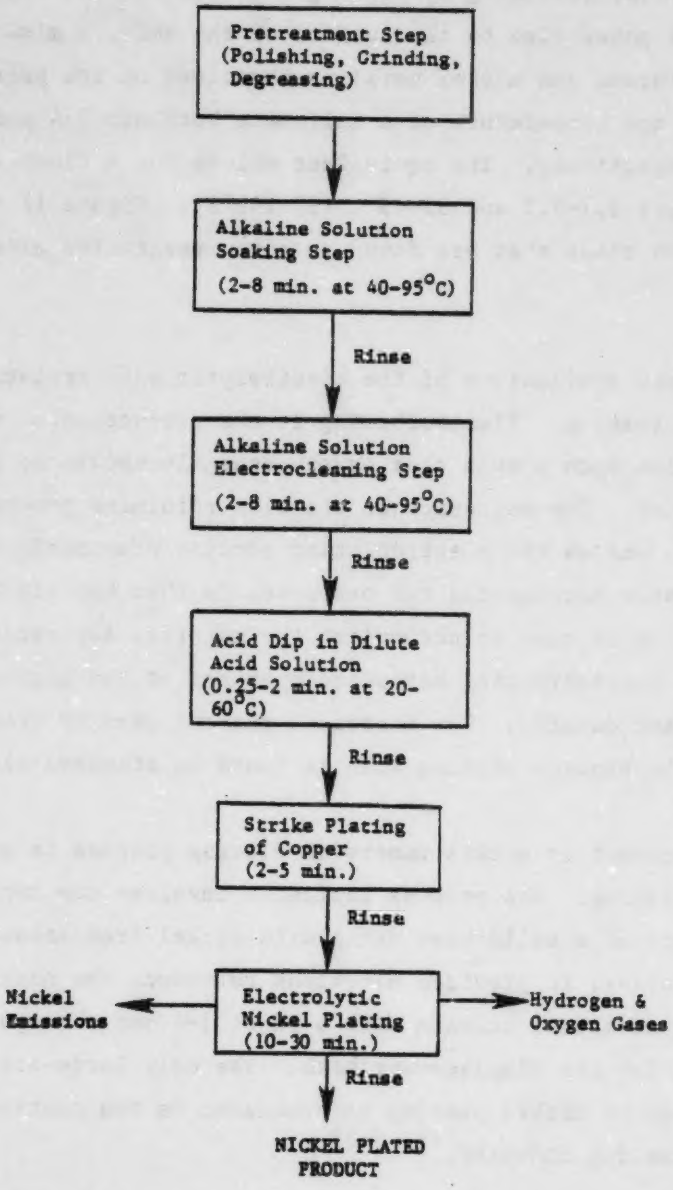

Pretreatment Step
(Polishing, Grinding, Degreasing)
Alkaline Solution Soaking Step
(2-8 min. at 40-95°C)
Rinse
Alkaline Solution Electrocleaning Step
(2-8 min. at 40-95°C)
Rinse
Acid Dip in Dilute Acid Solution
(0.25-2 min. at 20-60°C)
Rinse
Strike Plating of Copper
(2-5 min.)
Rinse
Nickel Emissions
Electrolytic Nickel Plating
(10-30 min.)
Hydrogen & Oxygen Gases
Rinse
NICKEL PLATED PRODUCT

Figure 17. Flow diagram for a typical nickel electroplating process.[48-51]

nickel-phosphorus alloy. The plating is performed through the controlled autocatalytic reduction of cations (Ni^{++}) at the surface of the base metal. Hypophosphite anions [$(H_2PO_2)^-$] in an aqueous medium are employed as reducing agents, and no external electric current is used. The probable chemical reactions occurring during plating can be represented by the following equations:

$$(H_2PO_2)^- + H_2O \xrightarrow{\text{(Catal. Ni)}} H^+ + (HPO_3)^{--} + 2H\ (\text{Catal.}) \qquad (1)$$

$$Ni^{++} + 2H(\text{Catal.}) \longrightarrow Ni^{\circ} + 2H^+ \qquad (2)$$

$$(H_2PO_2)^- + H(\text{Catal.}) \longrightarrow H_2O + OH^- + P \qquad (3)$$

$$(H_2PO_2)^- + H_2O \xrightarrow{\text{(Catal. Ni}^{\circ})} H^+ + (HPO_3)^{--} + H_2$$

Active hydrogen atoms, after being loosely bonded by the catalyst (Equation 1), reduce the nickel ions to metallic nickel while they are being oxidized to hydrogen ions (Equation 2). Simultaneously, a small portion of the hypophosphite anions are similarly reduced by active hydrogen and adsorbed on the catalytic surface, yielding elemental phosphorus, water, and hydroxyl ions (Equation 3). The hypophosphite reducing anions are also catalytically oxidized to acid orthophosphite anions, with the evolution of hydrogen gas (Equations 1,4).[48-51]

Emission Factors

Nickel emissions potentially occur from nickel plating shops during the handling of nickel salts used to prepare plating baths, the plating of nickel, and grinding, polishing, and cutting operations performed on the finished product and scrap metal. Emissions of nickel from the handling of nickel salts are fugitive in nature and are generally contained within the occupational environment. During electrolytic nickel plating, hydrogen and oxygen gases can be generated such that nickel salts from the plating bath can be entrained and emitted as a mist. Nickel emissions from misting are generally very low or nonexistent due to the low temperature and low current densities used in nickel plating baths.[48-51] Most nickel emissions generated in this manner probably remain in the workplace area. Potentially the largest amount of nickel emissions from nickel plating would occur during grinding, polishing, and cutting operations performed on plated products and scrap metal. These operations displace metallic nickel particles into the occupational environment with atmospheric release being possible as a result of work area ventilation. In all instances in the literature, nickel air emissions are reported as negligible.[26,47,52] No emission factors for nickel air emissions from electroplating are given.

Source Locations

An extensive, though incomplete, listing of nickel electroplating facilities is given in Table 6 of Section 3. Published directories of manufacturing firms may be used to identify more nickel electroplaters within SIC code 3471, Electroplating, Plating, Polishing, Anodizing and Coloring. Names and locations of nickel electroplaters may also be available from the membership roll of the technical group known as the American Electroplaters' Society, Inc.

Battery Manufacturing

Process Description

The primary use of nickel in the battery manufacturing industry is in the production of nickel-cadmium (Ni-Cd) batteries. Nickel is used in Ni-Cd batteries as the active material for the positive electrode and as a binder for some types of battery plate construction. Nickel use in another type of battery, the nickel oxide-zinc storage battery, is expected to grow in the near future as the technology for electric vehicles develops. One plant producing nickel oxide-zinc batteries is scheduled to go on line in the mid 1980's.[53-67]

Batteries consist of one or more cells. There are two major cell categories known as sealed cells and vented cells. Batteries constructed with sealed cells commonly have small cylindrical, rectangular, or button configurations which have application in calculators, toys, radios, and other types of consumer products. Even though they are classified as sealed, most sealed cell batteries have a safety vent to relieve pressure within the cell if gas builds to a near-explosive level.[53-67] In contrast, vented cell batteries are designed to release gases as part of their normal operation. Vented cells are filled with excess electrolyte and are suitable for constant charging/discharging and applications where the orientation of the battery can be maintained.

Sealed and vented Ni-Cd battery cells can be made by similar processes. In each, negative and positive electrodes are assembled alternately with a separator between the electrodes to hold the electrolyte in place and to isolate the negative and positive electrodes. Minor assembly differences between manufacturers may be noted.

Although the production of the overall Ni-Cd cells is similar throughout the industry, the production of the cell electrode plates is not. Two basic types of electrode plate construction are found in the U. S., sintered plate and pocket plate. Because sintered plate construction predominates in the U. S., it is discussed in detail in the following process description.

The sintered plate process basically involves binding of the cell's active materials to the nickel-plated base structure. In the process, binder materials such as nickel powder are heated to very high temperatures causing the contact points of each grain to weld together. This mechanism provides a very porous medium which is bound to the base structure. The void space in the binder material is then impregnated with nickel and cadmium nitrate salts (active material) by soaking the sintered base in either a nickel or cadmium salt solution. The impregnated plate is then submerged in a potassium hydroxide solution causing the nickel and cadmium nitrate to convert to the hydroxide form. The plate material is then washed, dried in an oven, and cut into individual plates for cell assembly. Figure 18 presents a flow diagram of this impregnation process and the major operations involved in Ni-Cd battery manufacture.

Emission Factors

The forms of nickel most likely to be emitted by a Ni-Cd battery plant are metallic nickel, nickel oxide, nickel nitrate, and nickel hydrate. All nickel compounds emitted by Ni-Cd battery plants are in the form of particulate matter. Emissions of metallic nickel powder in the manufacturing of Ni-Cd batteries are primarily fugitive in nature as a result of material handling and transfer operations. Fugitive emissions of this type occur mainly in connection with sintering operations performed during battery plate production. Process nickel emissions from the sintering operation exist primarily as nickel oxide since during sintering metallic nickel powder is subjected to very high oxidizing temperatures in order to cause the contact points of each grain to weld together.

Fugitive emissions of nickel nitrate from material handling and processing operations are possible during the preparation of nickel salt impregnation solutions used in electrode plate production. Nickel hydrate emissions from the production of Ni-Cd batteries also occur during plate formation. When the nickel nitrate impregnated plate is submerged in a potassium hydroxide solution, nickel nitrate is converted to the hydroxide form. As water is evaporated from the nickel hydroxide material during the drying operation, nickel hydrate crystals are formed and emitted. Fugitive nickel hydrate particles can also be emitted during the plate cutting operation.

There are no organized estimates available on the level of nickel being emitted into the air nationally from Ni-Cd battery plants. Emissions are

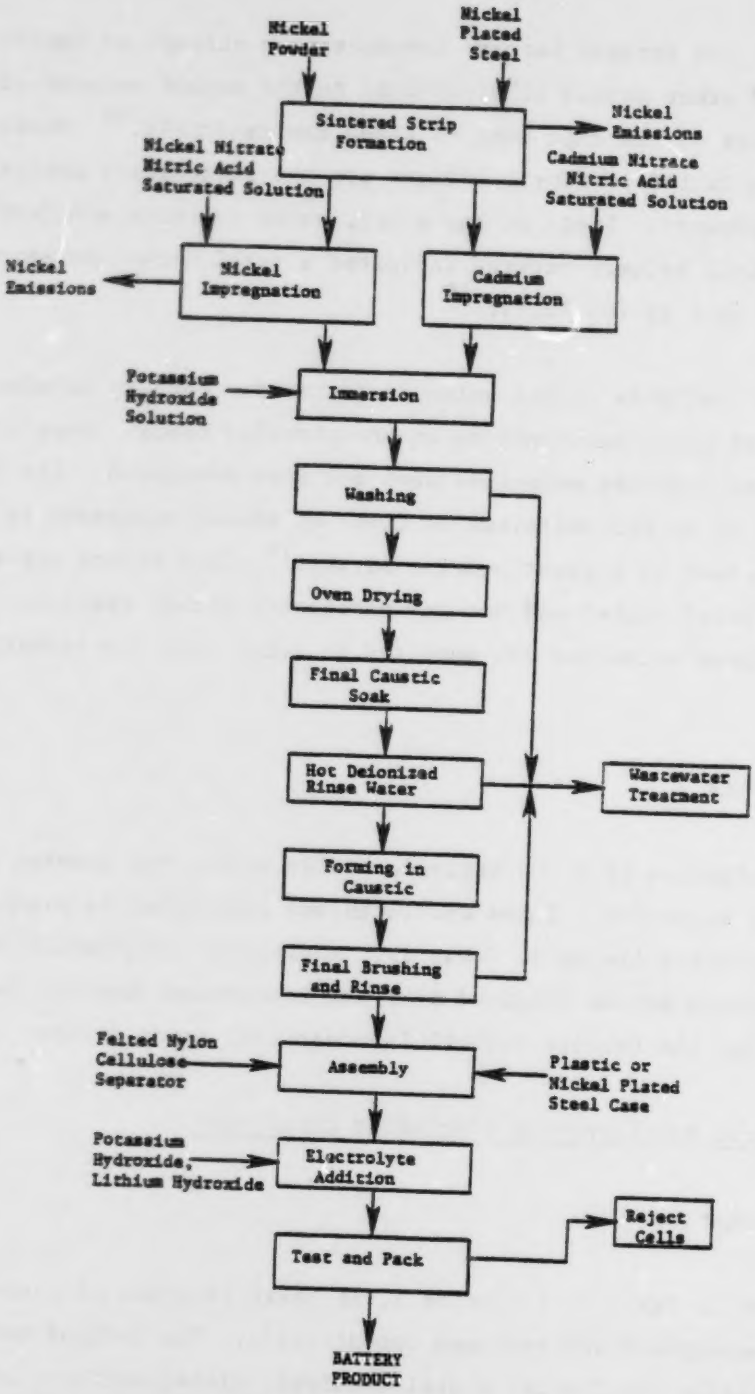

Nickel Powder
Nickel Plated Steel
Sintered Strip Formation
Nickel Emissions
Nickel Nitrate
Nitric Acid
Saturated Solution
Cadmium Nitrate
Nitric Acid
Saturated Solution
Nickel Emissions
Nickel Impregnation
Cadmium Impregnation
Potassium Hydroxide Solution
Immersion
Washing
Oven Drying
Final Caustic Soak
Hot Deionized Rinse Water
Wastewater Treatment
Forming in Caustic
Final Brushing and Rinse
Felted Nylon Cellulose Separator
Assembly
Plastic or Nickel Plated Steel Case
Potassium Hydroxide, Lithium Hydroxide
Electrolyte Addition
Reject Cells
Test and Pack
BATTERY PRODUCT

Figure 18. Flow diagram of typical production operations in impregnation sintered plate nickel-cadmium battery manufacture. 53-70

expected to be low because battery manufacturers attempt to control nickel emissions (and other metals like cadmium) to the extent economically possible because of the high cost of these raw materials.[68] Hooding and vacuum systems ducted to fabric filters are the predominant control methods used in the industry. Tests at one plant, which controls a majority of the sealed cell Ni-Cd battery market, indicated a total nickel emission level of approximately 28.1 kg (62 lb)/yr.[69]

The only available nickel emission factor for battery manufacturing describes total plant emissions on an uncontrolled basis. Separate factors for process and fugitive emissions have not been developed. The factor of 4 kg (8.8 lb) of nickel emissions/Mg (ton) of nickel processed is based on industry responses to a questionnaire survey.[26] This factor expresses emissions as total nickel and not any particular nickel species. The majority of these emissions are expected to occur from the sintering operation.

Source Locations

The manufacture of Ni-Cd batteries falls within the general SIC code 3691, Storage Batteries. Those manufacturers identified as producers of Ni-Cd batteries are listed in Table 19. Additional information on Ni-Cd battery producers may be obtained from the Independent Battery Manufacturers Association and the Battery Council International trade groups.

Nickel Chemical Manufacturing (Including Catalysts)

Process Description

As shown in Table 7 of Section 3, at least 28 types of nickel chemicals (including catalysts) are produced domestically. The largest volume and most commercially significant nickel chemical, nickel sulfate, has the greatest potential for nickel air emissions because its production consumes

TABLE 19. NICKEL-CADMIUM BATTERY MANUFACTURERS IN THE UNITED STATES[53-67]

Company	Location
General Electric	Gainesville, FL
Gould[a]	St. Paul, MN
Union Carbide	Cleveland, OH
Saft America	Valdosta, GA
Marathon Battery	Waco, TX
McGraw Edison	Greenville, NC
NIFE	Lincoln, RI
Eagle-Picher	Colorado Springs, CO

[a] Recently purchased by Saft America, announced plans are to shut down the nickel-cadmium battery operations.

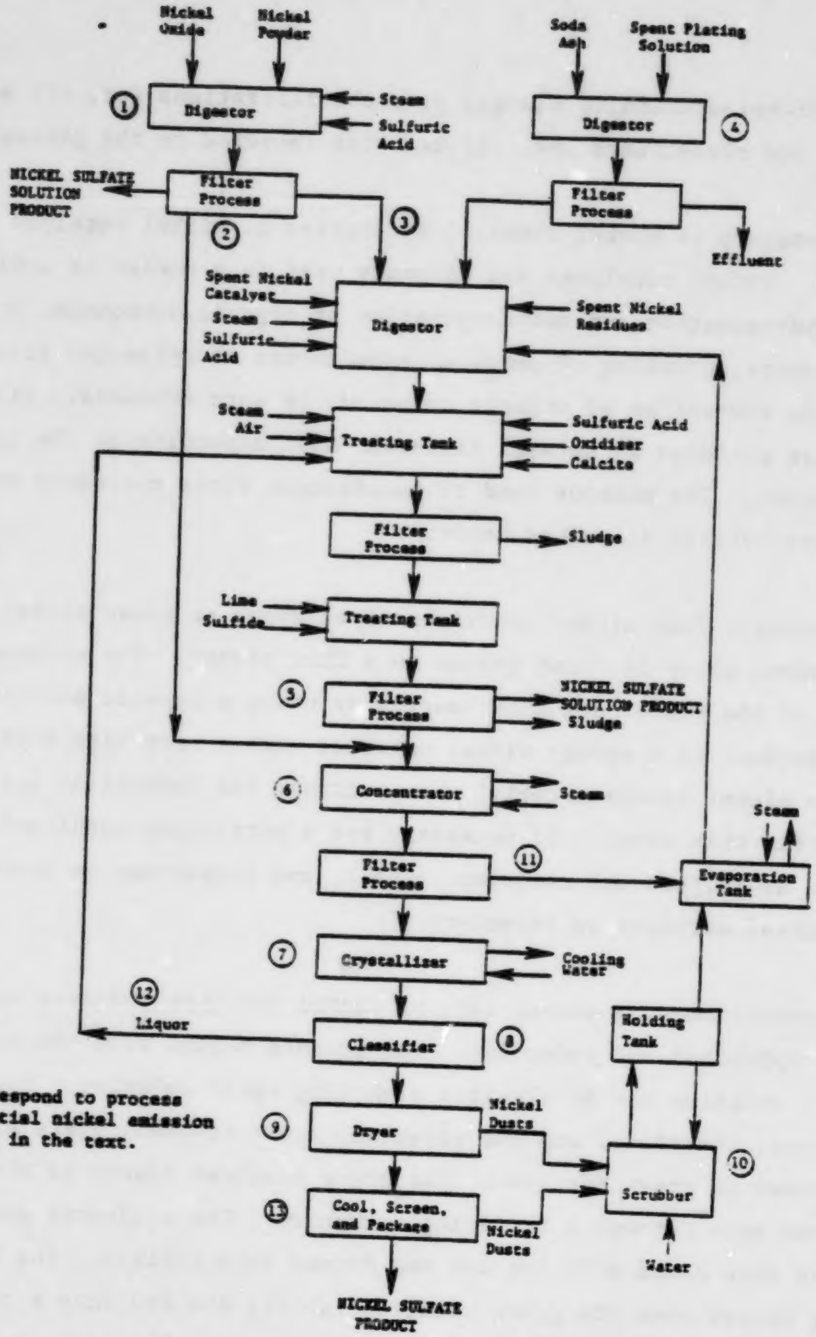
NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of nickel emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

the largest quantity of nickel raw material.[71] Nickel sulfate production is, therefore, described below to illustrate a representative nickel chemical manufacturing process.

Figure 19 illustrates a representative process flow diagram for a nickel sulfate production facility.[71] Nickel sulfate can be produced from several raw materials: pure nickel powder, nickel oxide, or spent nickel-plating solutions. If pure nickel or nickel oxide is used, the first step of the process involves dissolving the nickel compound in sulfuric acid (pt. 1, Figure 19). For a different nickel salt, such as nickel chloride, a different acid solvent would be used such as hydrochloric acid. The resulting solution is filtered (pt. 2) and either packaged as a product, or processed further to recover the solid nickel sulfate hexahydrate. The sludges produced by filtration can also be further processed (pt. 3) to generate additional nickel sulfate.[71]

When spent nickel-plating solutions are used as the starting raw material, digestion with sulfuric acid is the initial step in the nickel sulfate process (pt. 4). In a series of subsequent steps, the resulting solution is treated with oxidizers, lime, and sulfides to remove impurities. The purified nickel sulfate solution is filtered and sold or processed further to generate a solid nickel sulfate product.[71]

To recover the solid product in either the spent nickel-plating solution process or the pure nickel process, the nickel sulfate solution is first concentrated (pt. 6). After concentration, the soluton is filtered again and sent to a crystallizer (pt. 7). The product of the crystallization process is fed to a classifier (pt. 8) where the solid nickel sulfate product is recovered. To facilitate final packaging, the nickel sulfate is dried (pt. 9), cooled, and screened. Nickel sulfate dusts generated during drying are generally controlled by wet scrubbers, with the resulting nickel-containing scrubber water being recycled to the process


Nickel Oxide
Nickel Powder
Steam
Sulfuric Acid
①
Digestor
NICKEL SULFATE SOLUTION PRODUCT
Filter Process
②
③
Soda Ash
Spent Plating Solution
Digestor
④
Filter Process
Effluent
Spent Nickel Catalyst
Steam
Sulfuric Acid
Digestor
Spent Nickel Residues
Steam
Air
Treating Tank
Sulfuric Acid
Oxidizer
Calcite
Filter Process
Sludge
Lime
Sulfide
Treating Tank
⑤
Filter Process
NICKEL SULFATE SOLUTION PRODUCT
Sludge
⑥
Concentrator
Steam
Steam
Filter Process
⑪
Evaporation Tank
⑦
Crystallizer
Cooling Water
⑫
Liquor
Classifier
⑧
Holding Tank
⑨
Dryer
Nickel Dusts
Scrubber
⑩
⑬
Cool, Screen, and Package
Nickel Dusts
Water
NICKEL SULFATE PRODUCT

***Numbered points correspond to process operations and potential nickel emission streams as discussed in the text.**

Figure 19. Representative process flow diagram for the production of nickel sulfate.[71]

(pt. 10). Nickel-containing sludges from the filtrations (pt. 11) and the liquor from the classifiers (pt. 12) are also recycled to the process.[71]

A subcategory of nickel chemical production is nickel catalyst manufacture. Nickel catalysts are commonly used in a number of applications including hydrogenation and dehydrogenation of organic compounds, artificial aging of liquors, cracking of ammonia, manufacture of hydrazine from urea, and catalytic combustion of organic compounds in auto exhausts. Nickel catalysts are produced in several different ways depending on the type of catalyst needed. The methods used to manufacture three currently used catalysts are briefly described below.

To produce a fine nickel powder catalyst known as Raney nickel, a nickel-aluminum alloy is first ground to a fine powder. The aluminum components of the powder are then leached by using a caustic solution. The resulting product is a spongy nickel material with a very high surface area. To make the nickel sponge material more suitable for industrial application, it is slurried with water. If necessary for a particular application, other metals such as molybdenum, chromium, cobalt, and copper may be incorporated into the nickel catalyst as promoters.[72-75]

The production of a second type of nickel catalyst involves two major steps, precipitation and reduction. The process begins with the mixing of a nickel salt solution and an alkaline promoting agent solution. Upon mixing the solutions, the nickel and the promoting agent co-precipitate as a material known as green catalyst. The green catalyst slurry is then agitated and sent through a filtering mechanism. The collected green catalyst is then dried with hot air and formed into tablets. The final processing occurs when the green catalyst tablets are fed into a reactor and reduced at high temperature with steam and hydrogen. The product nickel catalyst is then slurried in vegetable oil and packaged for use.[72-75]

In the manufacture of supported nickel catalysts, the starting material is generally nickel powder or briquettes. In preparation for adsorption onto the support medium, the catalyst material is ionized and solubilized. The nickel catalyst is then adsorbed onto a support medium which may be alumina or some other refractory material. The supported nickel catalyst is then oxidized to complete the preparation process. In some instances this technique is modified so that prepared nickel oxide is combined directly with a support medium.[72-75]

Emission Factors

In the production of nickel sulfate (Figure 19) the primary points of potential nickel (or nickel compound) emissions are the nickel powder/nickel oxide handling and preparation steps (pt. 1, Figure 19), the solid nickel sulfate drying operation (pt. 9), and the nickel sulfate packaging operation (pt. 13). The emissions from nickel powder/nickel oxide handling and nickel sulfate packaging are primarily fugitive dusts caused by material displacement. Local exhaust hooding is used to collect these dusts. The collected nickel material is either sent to a control device (wet scrubber or fabric filter) from which it can eventually be recycled to the process or vented to the atmosphere. Nickel sulfate emissions from the product dryers are also collected and directed to wet scrubbers or fabric filters for control. Again, the collected nickel material is usually recycled to the process. Though other nickel chemical plants may have slightly different configurations from those shown in Figure 19, materials handling and product drying are expected to be the primary sources of potential nickel emissions in each facility.

In the production of nickel catalysts, nickel preparation and handling steps are the most significant sources of nickel emissions.[72-75] Crushing, grinding, and screening of nickel prior to catalyst production all generate nickel dust emissions. The emission control techniques applied in the catalyst operations are very similar to those used in the basic nickel chemical processes. Local exhaust hooding is used to capture and convey nickel emissions to a scrubber or fabric filter particulate control device.[72-75]

Available references report that nickel emissions from nickel chemical or nickel catalyst production processes are negligible.[26,71-75] In all cases either no nickel emission factors were given or they were listed as being negligible.[26]

Source Locations

The domestic producers of basic nickel chemicals are presented in Table 7 of Section 3. This list represents the population of nickel chemical producers as of mid 1982. A partial listing of nickel catalyst producers is given in Table 20. This list was taken from the Thomas Register of Manufacturers and the McGraw-Hill Chemical Buyers' Guide. Only catalyst manufacturers specifically noted as producing nickel catalysts are reported.

INDIRECT SOURCES OF NICKEL

Coal and Oil Combustion

Process Description

Nickel is a trace element common in most coals and oils. Tables 21 and 22, respectively, summarize the nickel contents of typical coals and oils used in this country. The average nickel content of U. S. coals ranges from about 5 to 21 ppm, whereas the average nickel content of U. S. crude oils is 15 ppm. Residual oils appear to have higher nickel contents, on the average, than crude oils as a result of the refining process. A heavy metal such as nickel has a very low vapor pressure and exists as a low vapor

TABLE 20. NICKEL CATALYST PRODUCERS[19,76,77]

Company	Location
United Catalyst	Louisville, KY
Union Carbide	Tarrytown, NY
American Cyanamid	Wayne, NJ
De Gussa	Teterboro, NJ
Davison Div. of W. R. Grace	Baltimore, MD
Mallinckrodt, Inc.	Erie, PA
Harshaw Chemicals	Cleveland, OH
Activated Metals & Chemicals	Sevierville, TN
Houdry Div. of Air Products & Chemicals	Allentown, PA

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of nickel emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

TABLE 21. TYPICAL NICKEL CONTENT OF DOMESTIC COALS[78]

Coal Source	Average Nickel Content, ppm	Range of Nickel Content, ppm
Eastern United States (Appalachia)	15	6.3 - 28
Midwestern United States (Illinois Basin)	21	7.6 - 68
Western United States	5	1.5 - 18[a]
Average of Total U.S.	20	3 - 80

[a] Data presented in reference 79 show measured nickel levels in an unwashed and washed western coal to be 100 ppm and 170 ppm, respectively.

TABLE 22. NICKEL CONTENT OF VARIOUS CRUDE AND FUEL OILS[26,81-84]

Oil Source/Type	Average Nickel Content, ppm	Range of Nickel Content, ppm
United States/crude	15	1.4 - 64
Foreign/crude	25.6	1.8 - 59
United States/residual No. 6	48.5[a]	NA[b]
United States/residual No. 5	31	NA
United States/residual No. 4	18	NA
Foreign/residual No. 6	36.3	4 - 61.2
United States/distillate No. 2	NA	< 0.02 - 1.7

[a] Reference 86 indicates that this value is probably accurate for regular sulfur fuel oil, but that it is too high for low sulfur fuel oil, the use of which became important around 1970. Low sulfur fuel oil has a total nickel content that averages 10 ppm. The two types of oil are used currently in roughly equal amounts.

[b] NA means data not available.

pressure organo-metallic complex with the higher molecular weight hydrocarbons in crude oil. As such, the metal concentrates in the heavy residual part of the crude as it is distilled.[80]

This concentration phenomena explains why nickel contents of distillate oils are generally much lower than residual and crude oils. In analytical tests of several distillate oils by a major oil refiner, nickel was not found at a limit of detection of 0.02 ppm.[81] Other measured values of nickel in distillate oil have ranged from < 0.1 ppm to 1.7 ppm.[82-84] In contrast, however, measured levels of nickel in some distillate oils have been as high as 23 ppm.[85] There are no data in the literature to reconcile this inconsistency, except that the analytical method used in these tests (spark source emission spectrometry) is known to sometimes encounter interferences when measuring nickel. These higher than expected values for nickel in distillate oil that have been reported may be the result of a faulty analytical procedure.[86]

The amount of nickel emitted to the atmosphere during coal and oil combustion is dependent primarily on the following factors:

- the nickel content of the fuel,
- the type of boiler used and its firing configuration,
- the partitioning of nickel between fly ash and bottom ash,
- the degree of nickel enrichment on fine fly ash, and
- the nickel removal efficiency of any controls that may be present.

The effect of each of these factors is described in the following paragraphs.

The concentration of nickel in coals and oils has been determined to be the major factor affecting uncontrolled nickel emissions from combustion sources.[87] The greater the nickel concentration in the fuel, the higher the uncontrolled rate of nickel emissions. For the combustion of coal, the type of boiler and its firing configuration both affect nickel emissions by affecting the amount of coal ash that ends up as bottom ash. The bottom ash contains some concentration of nickel that will not be emitted to the atmosphere. The combustion of oil produces essentially no bottom ash, minimizing the effect of boiler type and firing configuration on the level of nickel emissions from oil fuels.

The emission of nickel from coal or oil combustion is generally explained by the volatilization/condensation mechanism (VCM) theory. The theory basically states that, in the firebox of a boiler or furnace, peak temperatures of approximately 1650°C (3000°F) volatilize fuel elements such as nickel. The hot flue gases from the combustion process then undergo cooling through convective heat transfer and other mechanisms, condensing the volatilized species. Volatilized nickel may condense or adsorb onto existing particles in the exhaust stream according to the available particulate surface area, or may homogeneously condense into fine nickel-containing particles.[88] Through this procedure, the nickel concentration in the bottom ash is depleted, while the concentration in the fly ash is enriched.[7] This phenomenon occurs because the fly ash has more relative surface area for condensation than the bottom ash and because the bottom ash does not come in contact with the volatilized nickel long enough for it to condense.[88,89] As an example, tests of three coal fired utility boilers showed that 18 percent of the fuel nickel deposited in the bottom ash whereas 82 percent entrained onto the fly ash.[90]

The degree of partitioning and small particle enrichment that goes on during the volatilization and condensation of nickel has been studied by several researchers, especially for coal combustion. These researchers have devised several classification schemes to describe the partitioning and enrichment behavior of many trace elements, including nickel. One of the more simplistic, but useful classification systems is given below:[88,89]

- Class 1. Elements which are approximately equally distributed between fly ash and bottom ash, showing little or no enrichment onto small particles.
- Class 2. Elements which are enriched in fly ash relative to bottom ash, or show increasing enrichment with decreasing particle size.
- Class 3. Elements which are intermediate between Classes 1 and 2.
- Class 4. Elements which are emitted entirely in the gas phase.

Nickel emissions from coal combustion have been shown to demonstrate the behavior of Classes 1, 2, and 3, and are usually categorized under Class 3. Class 3 elements such as nickel are apparently not totally volatilized during the coal combustion process, and, therefore, exhibit a capability for bottom ash or fly ash deposition. Nickel emissions from oil combustion demonstrate the behavior of Class 2 elements, primarily because little bottom ash is produced in oil fired boilers.

Nickel emissions from both coal and oil combustion show preferential enrichment on fine fly ash particles.[89,91] Because of this enrichment factor, the type of control device used plays an important role in determining how much nickel is removed from the flue gas exhaust. Control devices not designed to remove fine particulates do not perform as well on nickel emissions as devices which are so designed. A summary is given in Tables 23-25 of the collection efficiencies for nickel that have been determined for ESPs, fabric filters, and wet scrubbers. In addition to control devices, fuel cleaning has also been shown to be an effective method of reducing nickel and other trace element emissions from combustion processes. Physical coal cleaning has been shown to remove from 12 to 50 percent of the nickel in coal, depending on the source of the coal. Physical cleaning is 40-50 percent efficient on eastern and midwestern coals, but is only 12 percent efficient on western coals. Hydrotreating processes are very effective at removing nickel from oil. Removal efficiencies of greater than 95 percent have been achieved.[92]

TABLE 23. NICKEL COLLECTION EFFICIENCIES FOR ELECTROSTATIC PRECIPITATORS[92]

Source Identification	Fuel	Percent Collection Efficiency
Power Plant A	Coal	96.3
Power Plant B	Coal	99.4
Power Plant C	Coal	99.7
Power Plant D	Coal	99.8
Power Plant E	Coal	98
Power Plant F	Coal	96.4
Power Plant G	Coal	98.7
Power Plant H	Coal	78.5

TABLE 24. NICKEL COLLECTION EFFICIENCIES FOR FABRIC FILTERS[92]

Source Identification	Fuel	Percent Collection Efficiency
Power Plant A	Coal	99.6
Power Plant B	Coal	100
Steel Mill	--	100

TABLE 25. NICKEL COLLECTION EFFICIENCIES FOR WET SCRUBBERS[92,93]

Source Identification	Fuel	Percent Collection Efficiency
Power Plant A	Coal	95[a]
Power Plant B	Coal	90.8 - 98[b]
Industrial Boiler A	Coal	95[c]
Industrial Boiler A	Oil	83[c]
Power Plant C	Coal	>97[d]

[a] Controlled by a venturi scrubber.

[b] Controlled by a horizontal scrubber.

[c] Scrubber was designed primarily for SO_2 control.

[d] The scrubber is preceeded by an ESP.

Emission Factors

Nickel emission factors for coal and oil combustion are presented in Tables 26 and 27. In both tables, calculated and measured emission factors are given. For oil combustion, calculated factors have been developed by determining the amount of nickel in the fuel and then by assuming that 100 percent of the nickel is emitted. This approach results in an emission factor that is theoretically the maximum for the fuel under analysis. The only means by which actual emissions could be greater than the calculated value are that nickel is added to the emission stream from metal erosion in the boiler or control device, or nickel is present in combustion air at a significant level. Calculated emission factors for oil combustion are generally much greater than the same factors determined by testing. In one series of tests, calculated nickel emission factors were consistently two times higher than what was determined by actual emissions testing.[85]

Calculated nickel emission factors for coal combustion also rely on the amount of nickel in the fuel as a primary input. The application of average nickel enrichment ratios (which have been estimated by testing) and average control device efficiencies are also an integral part of the calculation. For coal combustion, particularly sources controlled by an ESP, measured nickel emission factors were found to be greater than the amount of nickel that could be calculated to be emitted based on fuel nickel levels. This inconsistency again indicates an influx of nickel into the emission stream.[94] Measured nickel emission factors for oil and coal combustion are based on actual emissions generated during source testing and analysis of a boiler and a knowledge of the quantity and characteristics of the fuel burned.

As shown in Tables 26 and 27, wide variability exists in some of the emission factor estimates for coal and oil combustion. Although it is beyond the scope of this document to reconcile all the reasons for these large ranges, available data suggest that the most important factor

TABLE 26. NICKEL EMISSION FACTORS FOR OIL COMBUSTION[94-98]

Oil Type	Uncontrolled Nickel Emission Factors[f]	Type of Factor[c]
Domestic Crude	2 - 5 kg/10^6 liters (20 - 500 lb/10^6 gal)[a]	Calculated
Foreign Crude	20 kg/10^6 liters (200 lb/10^6 gal)[a]	Calculated
Residual #6	9.9 kg/10^6 liters (83 lb/10^6 gal)[a]	Measured
Residual #5	7.7 kg/10^6 liters (64 lb/10^6 gal)[a]	Measured
Residual #4	5.6 kg/10^6 liters (48 lb/10^6 gal)[a]	Measured
Residual (No. Unspecified)	63 - 1,056 pg/J[b]	Calculated
Residual (No. Unspecified)	57 - 63 pg/J[b,d]	Calculated
Distillate #2	0.046 - 0.049 kg/10^6 liters (0.38 - 0.41 lb/10^6 gal)[a,e]	Measured
Distillate #2	290 pg/J[b]	Measured
Distillate #2	13 - 446 pg/J[b]	Calculated

[a] Emission factor expressed as total nickel emitted per mass of oil fired.

[b] Emission factor expressed as total nickel emitted per unit of heat energy contained in the fuel.

[c] Calculated emission factors have been developed by determining the nickel content of the oil and making the assumption that all nickel in the fuel is emitted. Measured emission factors have been determined by actual emissions source testing and sample analysis combined with a knowledge of the amount of fuel burned.

[d] These emission factors represent controlled emissions. The 57 pg/J factor represents control with an ESP, while the 63 pg/J factor represents control with a scrubber.

[e] Reference 81 indicated the pg/J equivalent of this emission factor would be 1.25 - 1.35 pg/J, assuming that all the nickel present in the emissions came from the fuel. This factor is significantly lower than the other measured value for distillate oil combustion of 290 pg/J. This difference can basically be reconciled by examining the nickel content of the fuels burned. In the case of the lower emission factor, the fuel nickel level was about 0.05 ppmw. The fuel nickel content in the tests that produced the higher value ran as high as 23 ppmw.

[f] Nickel emissions from oil combustion[99-103] are most likely to exist as nickel sulfate, complex oxides of nickel and other metals, and nickel oxide.

TABLE 27. NICKEL EMISSION FACTORS FOR COAL COMBUSTION[79,82,91,92,94-96,98,104]

Coal Type	Boiler Type	Control Device[a]	Nickel Emission Factors, pg/J[b,d]	Type of Factor[c]
Anthracite	Stoker	None	135 - 470	Measured
Anthracite	Stoker	MC	29	Calculated
Anthracite	Pulverized	ESP	30	Calculated
Bituminous	Pulverized	None	130 - 2,900	Calculated
Bituminous	Pulverized	None	1,045	Measured
Bituminous	Pulverized	MC	709 - 870	Calculated
Bituminous	Pulverized	MC	16	Measured
Bituminous	Pulverized	ESP	50 - 62	Calculated
Bituminous	Pulverized	ESP	4.3 - 2,480	Measured
Bituminous	Pulverized	WS	213 - 227	Calculated
Bituminous	Pulverized	WS	0.48 - 133	Measured
Bituminous	Cyclone	MC	147	Calculated
Bituminous	Cyclone	ESP	2 - 11	Calculated
Bituminous	Cyclone	ESP	429 - 1,330	Measured
Bituminous	Cyclone	None	470	Measured
Bituminous	Cyclone	WS	38	Calculated
Bituminous	Cyclone	WS	20	Measured
Bituminous	Stoker	None	400 - 2,200	Calculated
Bituminous	Stoker	None	13 - 1,463	Measured
Bituminous	Stoker	MC	670	Calculated
Bituminous	Stoker	MC	13 - 2,230	Measured
Bituminous	Stoker	FF	71	Measured
Lignite	Pulverized	MC	228	Calculated
Lignite	Pulverized	MC	115 - 263	Measured
Lignite	Pulverized	ESP	8.3 - 13	Calculated
Lignite	Pulverized	ESP	< 68	Measured
Lignite	Pulverized	WS	161	Calculated
Lignite	Cyclone	ESP	4.5	Calculated
Lignite	Cyclone	ESP	< 47	Measured

TABLE 27. (CONTINUED) NICKEL EMISSION FACTORS FOR COAL COMBUSTION[79,82,91,92,94-96,98,104]

Coal Type	Boiler Type	Control Device[a]	Nickel Emission Factors, pg/J[b,d]	Type of Factor[c]
Lignite	Cyclone	WS	87	Calculated
Lignite	Cyclone	MC	221 - 320	Calculated
Lignite	Stoker	MC	276	Measured
Lignite	Stoker	ESP	< 38	Measured

[a] The key for the control device abbreviations is as follows:
MC - multicyclones
ESP - electrostatic precipitator
WS - wet scrubber
FF - fabric filter

[b] Emission factors expressed as total nickel emitted per unit for heat energy in the fuel.

[c] Calculated emission factors have been developed using average fuel nickel contents, average nickel enrichment ratios, and demonstrated average control device efficiencies. Measured emission factors have been determined by actual emissions source testing and sample analysis combined with a knowledge of the energy content of the fuel burned.

[d] Nickel emissions from coal combustion are most likely to exist as nickel sulfate, complex oxides of nickel and other metals, and nickel oxide.

influencing the situation is the nickel content of the fuel.[98] A problem of inconsistent information regarding fuel nickel levels was pointed out previously in connection with distillate oil.

Limited nickel emission factors are also available for the combustion of wood. In one set of tests for five furnaces burning wood, measured nickel emission factors ranged from 2-65 pg/J with the average being 29 pg/J. Other measured nickel emission factors for wood have ranged from a low of 3.6 pg/J to 110 pg/J.[82,96]

Several recent studies have produced results strongly indicating the forms of nickel occurring in emissions from coal and oil combustion. In fly ash samples collected from the stacks of five oil fired utility boilers, the nickel components were found to be 60-100 percent water soluble.[99] In the analysis of leachate from the solubility test, sulfate anion was the only anion present at more than trace levels. With this information it can be postulated that the form of nickel in the fly ash emissions and ambient air from oil fired combustion is predominantly nickel sulfate. This theory was eventually confirmed after the fly ash and the soluble and insoluble fractions of the samples were analyzed by Fourier transform infrared (FT-IR) spectroscopy.[100]

In another study of stack fly ash and scale samples taken from the reducing and oxidizing sections of an oil fired utility boiler, nickel was found to exist as nickel ammonium sulfate [$Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$].[101] These samples were analyzed by Raman spectroscopy. The water soluble fractions from the previous study (Reference 99) that determined nickel sulfate to be present were not analyzed for ammonium (NH_4^+). Therefore, the results from the Raman spectroscopy analysis do not necessarily conflict with those of Reference 99.

In the insoluble fraction of the fly ash samples from oil fired boilers, nickel was determined by X-ray diffraction (XRD) to potentially exist as nickel oxide.[99] However, with X-ray diffraction patterns it is frequently difficult to distinguish between pure nickel oxide and complex metal oxides involving nickel. In addition, nickel oxide is known to have an affinity for oxides of iron, aluminum, vanadium, and magnesium, all of which are compounds found in fly ash combustion products.[102] Potentially, the nickel component of the insoluble fraction could exist as complex nickel oxides such as ferrites, aluminates, and vanadates, a combination of complex metal oxides involving nickel and nickel oxide, or purely nickel oxide as the X-ray diffraction results.

The authors of Reference 99 have performed solubility and component analysis studies for fly ash from coal combustion similar to those discussed above for oil combustion. Samples of fly ash emitted from coal fired utility boilers controlled by electrostatic precipitation were water leached and the fraction of nickel found to be soluble ranged from 20-80 percent. For a boiler controlled by a limestone scrubber, 100 percent of the nickel present was found to be soluble.[99] As in the case of oil combustion, sulfate was the only major anion present, therefore, in the soluble fraction of fly ash from coal combustion, nickel probably exists as nickel sulfate. Various metal sulfates were identified in the soluble fraction of the coal combustion fly ash by XRD and FT-IR, but specific compounds were not reported.[99] The insoluble fractions of the coal fired combustion fly ash were determined by XRD to contain metal oxides, although neither nickel oxide nor complex oxides containing nickel were specifically indicated as being present. Considering the experience with the insoluble fraction of oil fired fly ash samples, it would be reasonable to expect that nickel oxides would be present in the insoluble fraction of coal fired fly ash.

Reference 103 examined the 100-200 μm size fraction of fly ash captured by electrostatic precipitators from coal fired utility boilers. Using magnetic separation and hydrochloric and hydrofluoric acid leaching steps, the fly ash was separated into a glass matrix, a mullite-quartz matrix, and a magnetic spinel matrix of composition $Fe_{2.3}Al_{0.7}O_4$. Analysis by XRD and

X-ray fluorescence (XRF) of the separated matrices indicated that approximately 90 percent of the nickel present was associated with the spinel. The theory was put forth that nickel probably existed as a substituted spinel of the form $Fe_{3-x}Ni_xO_4$.[103] Data gathered in this study reemphasized that while nickel is oxidized during the combustion process, it is probably not oxidized to pure nickel oxide.

Source Locations

Due to the large number of combustion sources in the U. S., individual source listings are not attempted here. However, data on the location of large emitters such as power plants and industrial boilers are available through published government data bases maintained by EPA and DOE, the Electric Power Research Institute (ERPI), and the American Boiler Manufacturers Association.

Cooling Towers at Electric Utility Stations

Wet cooling towers used by the electric utility industry are sources of nickel emissions because nickel-containing biocides and corrosion inhibitors, usually in the form of hydrated nickel sulfate salts, are used in the cooling tower water. In 1978 cooling towers were used for 20.6 percent of the total installed capacity for all power plants. Older, mechanical draft type towers comprise about 54 percent of the total tower population, while modern, closed-cycle type towers make up the remaining 46 percent.[98]

The emission of nickel from cooling towers is proportional to the water recirculation rate, the drift fraction (the fraction of cooling water emitted as drift droplets), the concentration of nickel in the cooling water (which is highly variable), and the ratio of the nickel concentration in the drift fraction to that in the cooling water.

The form of nickel emitted from cooling towers would vary depending on the concentration of ligands and anions in the water and on water quality (pH and hardness). Nickel sulfate is a Ni^{2+} species that is readily soluble in water. Therefore, nickel may be present in cooling tower drift emissions as the Ni^{2+} ion or bound to other ions such as hydroxide. If chlorine is also used to control biofouling, as is common practice, nickel chloride may be formed and emitted.

Nickel emission factors for utility cooling towers are presented in Table 28. These emission factors are based on measured emission rates obtained from tests of three utility cooling towers. The towers tested were designed for drift losses in the 0.1 to 0.2 percent range, which is representative of older, mechanical draft cooling towers. Estimates of nickel emissions from newer (closed-cycle) cooling towers with drift losses of 0.002 to 0.005 percent were obtained by a linear adjustment of the test results to reflect the lowered drift loss.[98]

Cement Production

Process Description

The production of cement is a potential source of nickel emissions because nickel can be a component of both the process feed materials and the fuels such as coal and oil that are burned in cement process kilns and dryers. In 1981, approximately 67.6 million Mg (75.1 million tons) of cement were produced in the U. S. Cement is produced by either a wet or dry method. In the dry method, feed materials are sent to the processing steps in a dry solid form. In the wet method, feed materials are mixed with water and sent to the processing steps as a slurry. Of the total domestic cement production, about 42 percent or 28.4 million Mg (31.2 million tons), is made by the dry method, and 58 percent, or 39.2 million Mg (43.9 million tons), by the wet method.[105]

TABLE 28. NICKEL EMISSION FACTORS FOR FRESH WATER UTILITY COOLING TOWERS[98]

Nickel Emission Factors, pg/J[a,b]	
Drift Loss Range of 0.1 to 0.2%	Drift Loss Range of 0.002 to 0.005%
16	0.34

[a] Emission factors are expressed as weight of pollutant per thermal energy input to the power plant associated with the cooling tower.

[b] Emission factors are based on source tests of three separate cooling towers.

The basic process flow diagram for cement production by the wet and dry methods is shown in Figure 20. The raw materials used to make cement can be divided into four basic categories: lime, silica, alumina, and iron. Approximately 1,600 kg (3,520 lb) of dry raw materials are required to produce 1 Mg (1.1 ton) of cement.[106] Following quarrying, raw materials are crushed to a suitable size for processing and are entered into either the wet or dry processing loop. In both wet and dry processes the materials are proportioned, ground, and blended prior to initiating the primary cement production steps.

In the dry process, the moisture content of the raw material is reduced to less than 1 percent either before or during the grinding operation. The dried materials are then ground to a powder, blended, and fed directly into an inclined rotary kiln. The powdered raw materials are fed into the upper end of the kiln and travel slowly to the lower end. The kilns are fired from the lower end so that hot gases pass upward and through the raw materials. Drying, decarbonating, and calcining are accomplished as the material travels through the heated kiln, finally burning to incipient fusion and forming what is known as clinker. The clinker is then cooled, mixed with about 5 percent gypsum by weight, and ground to a final product size. The cement product is then stored for packaging and shipment.[106]

In the wet process, a slurry is made by adding water to the raw materials at the initial grinding operation. After blending and mixing, excess water is removed and the slurry is adjusted to achieve the proper composition. The homogeneous mixture which is fed to the kilns is usually either a slurry of 30 to 40 percent moisture or a wet filtrate of about 20 percent moisture. The remaining kiln burning, clinker cooling, and gypsum addition steps are carried out the same as in the dry process.[106]

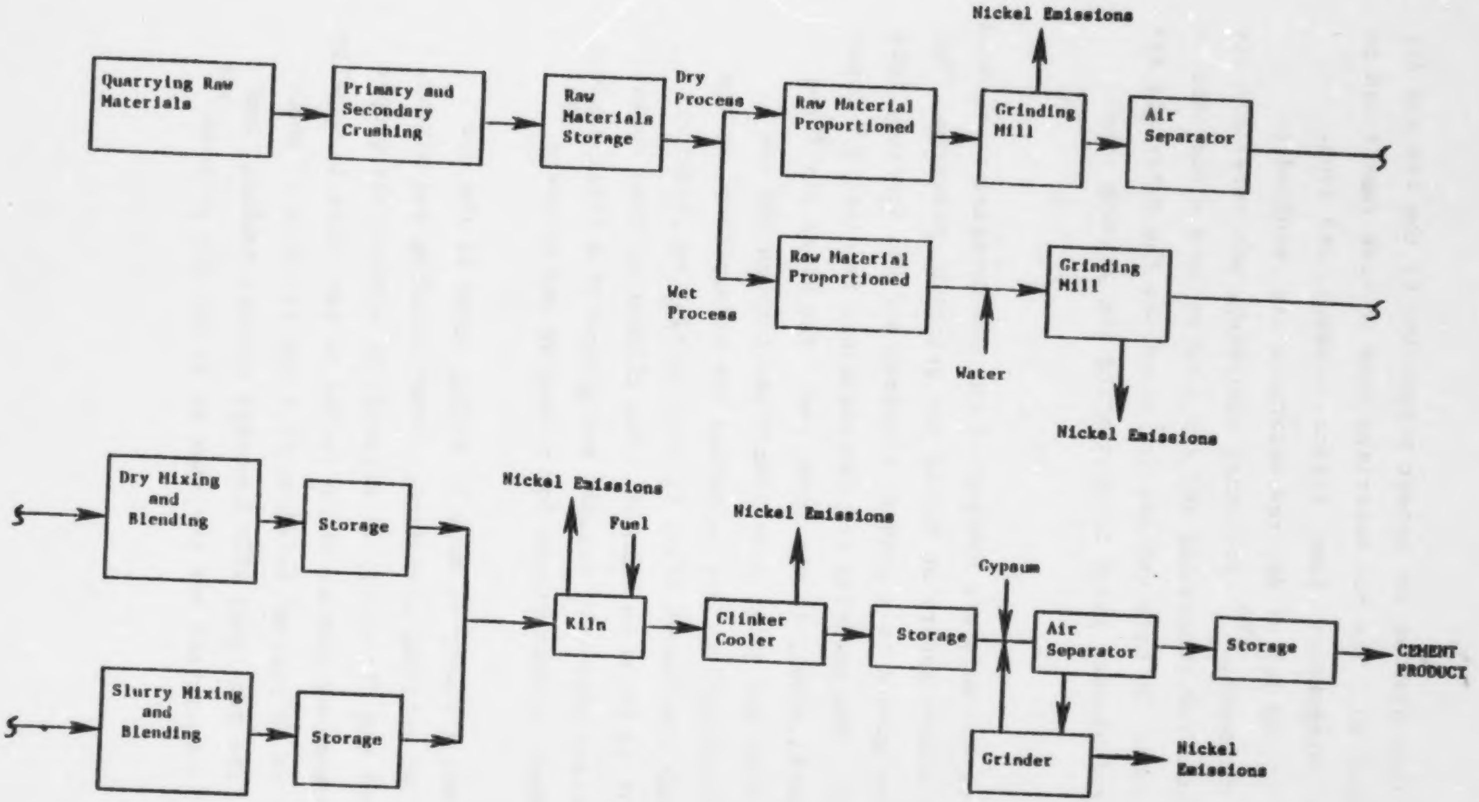

Quarrying Raw Materials
Primary and Secondary Crushing
Raw Materials Storage
Dry Process
Wet Process
Raw Material Proportioned
Grinding Mill
Air Separator
Nickel Emissions
Raw Material Proportioned
Water
Grinding Mill
Nickel Emissions
Dry Mixing and Blending
Storage
Slurry Mixing and Blending
Storage
Nickel Emissions
Fuel
Kiln
Nickel Emissions
Clinker Cooler
Storage
Gypsum
Air Separator
Storage
CEMENT PRODUCT
Grinder
Nickel Emissions

Figure 20. Basic process flow diagram for wet and dry cement production plants.[106]

Emission Factors

The primary nickel emission sources in cement production are the rotary kilns and grinding mills.[106] The majority of the cement industry uses controls such as multicyclones, ESPs, ESPs with cyclones, and fabric filters to reduce particulate, and consequently nickel emissions, from these sources. Typical collection efficiencies for control devices in these applications are:[106]

- multicyclones, 80 percent
- ESPs, 95 percent
- ESPs with cyclones, 97.5 percent
- fabric filters, 99.8 percent.

Nickel emission factors for wet and dry cement processes have been developed based on actual source testing of controlled cement plants. Table 29 summarizes the nickel emission factors for major cement plant sources.[26]

Few data were found which identified the nickel content of particles from cement processing. Nickel emitted from preliminary crushing and grinding would be in the same form as it is found in raw materials, most likely as a trace constituent of silicate minerals. Nickel emissions from kilns are probably in the forms of oxides of nickel and other metals, nickel oxide, and to a lesser extent nickel sulfate because of the high temperature, oxidizing conditions present in kilns. Nickel emissions from the clinker cooler would be in the same forms as those emitted from the kilns because the nickel particles would not be undergoing any reactions in the cooler. During milling and packaging, nickel would also be emitted in the forms that are produced in the kiln. Nickel emitted from the combustion of fossil fuels and dryers should be in the forms of nickel sulfate, complex oxides of nickel and other metals, and nickel oxide, as discussed previously in the combustion section.

TABLE 29. NICKEL EMISSION FACTORS FOR MAJOR CEMENT PLANT SOURCES[26]

Source Category	Controlled Nickel Emission Factors, kg/10^3 Mg (lb/10^3 tons)[f,g]
Dry Cement Process[a]	
Kiln[c,i]	0.2 (0.3)
Feed to Initial Grinding Mill[c,h]	0.005 (0.01)
Air Separator After Initial Grinding Mill[c,h]	0.0005 (0.001)
Raw Material Grinding Mills[c,h]	0.0003 (0.0006)
Feed to Finish Grinding Mill[c,i]	0.005 (0.01)
Air Separator After Finish Grinding Mill[c,i]	0.002 (0.006)
Wet Cement Process[b]	
Kiln[d,i]	0.1 to 1 (0.2 to 2)
Clinker Cooler[c,i]	0.002 (0.004)
Clinker Cooler[d,i]	0.05 (0.1)
Clinker Cooler[e,i]	0.1 (0.2)
Finishing Grinding Mill After Air Separator[c,i]	0.002 (0.004)

[a] Emission factors based on source testing of two plants with particulate sample analysis by emission spectroscopy.

[b] Emission factors based on source testing of three plants with particulate sample analysis by spark source mass spectrograph and optical emission spectrograph.

[c] Source controlled by a fabric filter.

[d] Source controlled by an ESP.

[e] Source controlled by two fabric filters in parallel.

[f] All factors expressed in terms of the amount of raw material feed input.

[g] Emission factors are expressed as total nickel.

[h] Nickel emissions from this source would be in the form of nickel silicate minerals.

[i] Nickel emissions from this source are expected to be in the forms of complex oxides of nickel and other metals, nickel oxide, and to a lesser extent nickel sulfate.

Source Locations

In 1981 there were 201 cement plants in the United States. The majority of plants were located in California, Texas, Pennsylvania, Michigan, and Missouri.[105] Individual plant locations can be determined from a variety of sources including:

- cement trade associations (e.g., Portland Cement Association)
- published industrial directories (e.g., Thomas Register, Standard & Poor's)
- the EPA National Emissions Data System (NEDS).

For sources indexed by SIC code, SIC 3241 should be used for cement manufacturing.

Municipal Refuse and Sewage Sludge Incineration

Process Description

Nickel is released during the incineration of municipal refuse and wastewater sewage treatment sludge because these materials contain varying quantities of nickel. The nickel content of municipal refuse ranges from 4-50 ppm, with an average content being 15 ppm.[107,108] Dry sewage treatment sludges have nickel contents ranging from 0-2800 ppm, with the average content equalling about 410 ppm.[109] A description follows of the workings of refuse and sewage sludge incinerators and of factors affecting nickel emissions.

The majority of municipal refuse incinerators have either refractory-lined or water-walled combustion chambers that are equipped with a grate upon which refuse is burned. The grate can be stationary, travelling, or vibrating, depending on the design of the incinerator. In most cases, natural draft or slight induced draft is used to pull air up through the grate to carry out the primary refuse combustion process. The combustion gases from the primary chamber pass through a flame port where they are reheated and mixed with air to achieve more complete oxidation. Exhausts from the secondary combustion chamber are either vented directly to the atmosphere or to a control device. The basic configuration of a representative municipal refuse incinerator is given in Figure 21.[110]

Sewage sludge incineration refers to the oxidation of sludge material generated by wastewater sewage treatment plants. The most prevalent types of incinerators for sludge oxidation are multiple-hearth and fluidized-bed units. Multiple-hearth incinerators are relatively simple pieces of equipment, consisting of a steel shell lined with refractory. The interior of the incinerator is divided by horizontal brick arches into separate compartments or hearths. Alternate hearths are designed with openings to allow solid material to drop onto the hearth below. At the center of the unit, a shaft rotates rabble arms that are located on each hearth. To enable the incinerated material to move inward and then outward on alternate hearths, teeth on the rabble arms are placed at an angle. As sludge is fed through the roof of the incinerator, the rotating rabble arms and rabble teeth push the material across the hearth to drop holes where it falls to the next hearth. This process continues until the sterile ash produced by the oxidation steps is discharged from the bottom of the incinerator. Figure 22 presents a schematic diagram of a typical multiple-hearth sewage sludge incinerator.[111]

The majority of multiple-hearth incinerators have three distinct operating zones. The first zone includes the top hearths where the water-laden sludge feed is partially dried by rising hot combustion gases. The second operating zone is the incineration/deodorization zone where temperatures of 760-980°C (1400-1800°F) are reached and maintained. The third zone of the multiple-hearth unit is the cooling zone where hot ash from incineration releases heat to incoming combustion air. The design temperature profile of a typical multiple-hearth incinerator is given in Table 30 to illustrate the break in operating zones.[112]

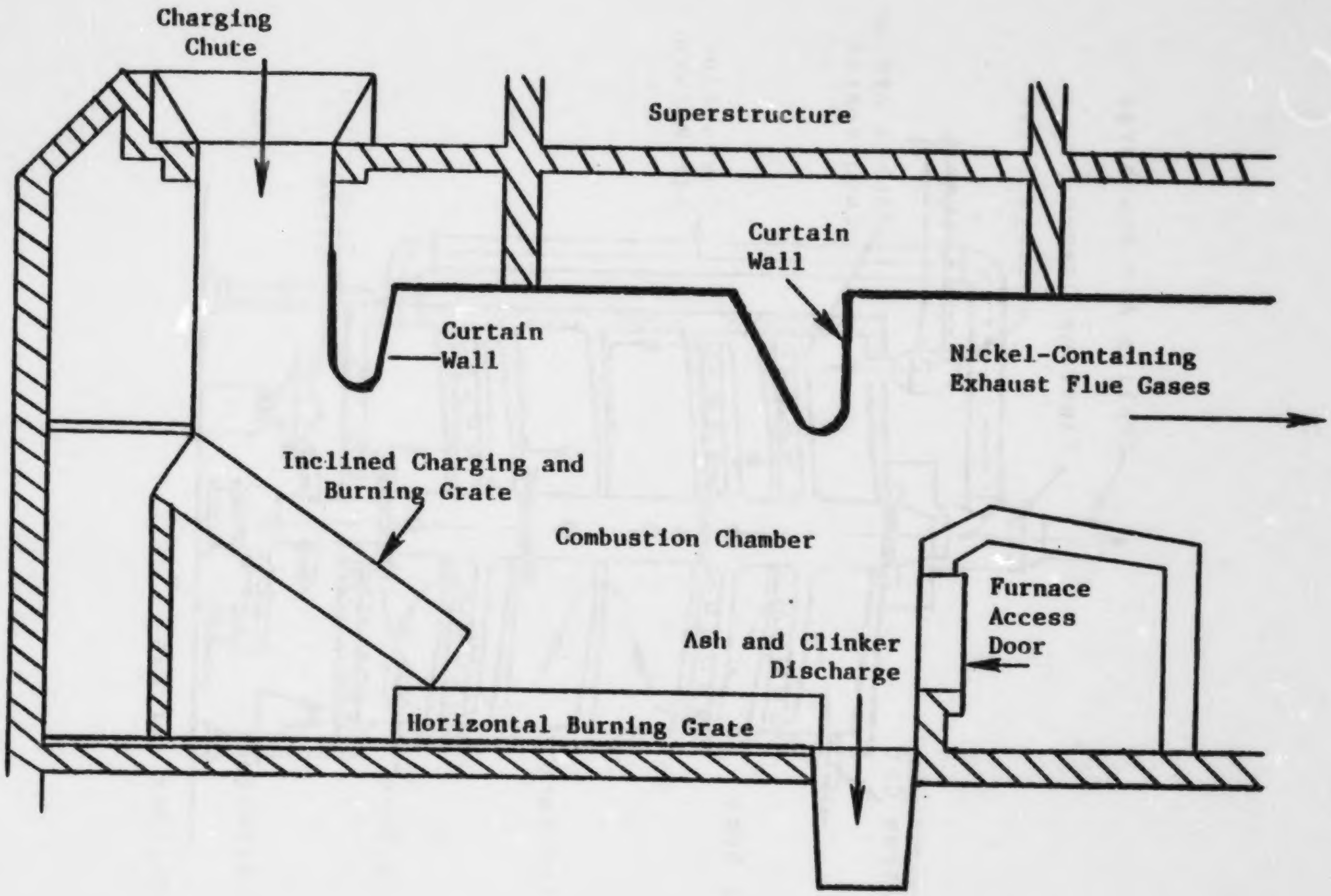

Charging Chute
Superstructure
Curtain Wall
Curtain Wall
Nickel-Containing Exhaust Flue Gases
Inclined Charging and Burning Grate
Combustion Chamber
Furnace Access Door
Ash and Clinker Discharge
Horizontal Burning Grate

Figure 21. Basic configuration of a municipal refuse incinerator.[110]

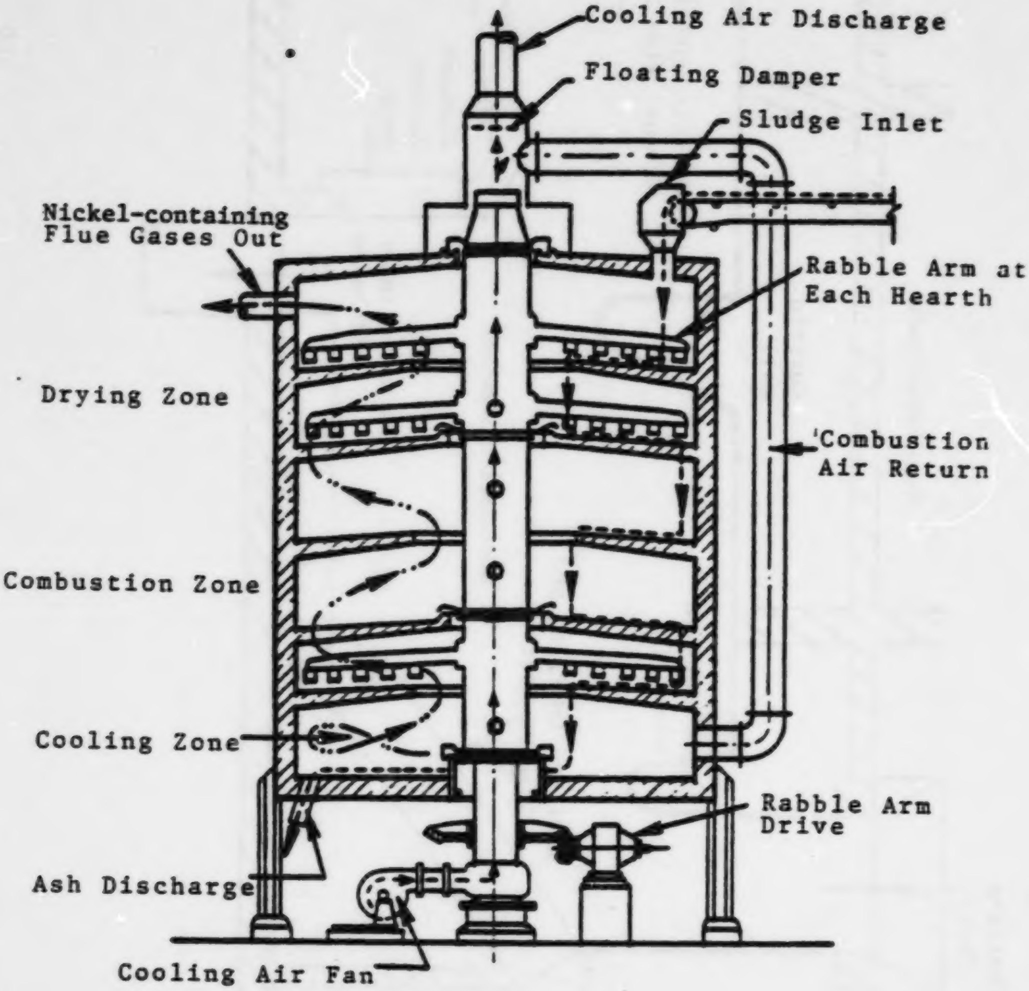

Cooling Air Discharge
Floating Damper
Sludge Inlet
Nickel-containing Flue Gases Out
Rabble Arm at Each Hearth
Drying Zone
Combustion Air Return
Combustion Zone
Cooling Zone
Rabble Arm Drive
Ash Discharge
Cooling Air Fan

Figure 22. Schematic diagram of a typical multiple-hearth sewage sludge incinerator.[111]

TABLE 30. DESIGN TEMPERATURE PROFILE OF A SEWAGE SLUDGE MULTIPLE HEARTH FURNACE[112]

Furnace Hearth No.[a]	Nominal Design Capacity, °C (°F)
1 (Sludge drying zone)	427 (800)
2	649 (1200)
3	900 (1650)
4	788 (1450)
5	649 (1200)
6 (Ash cooling zone)	149 (300)

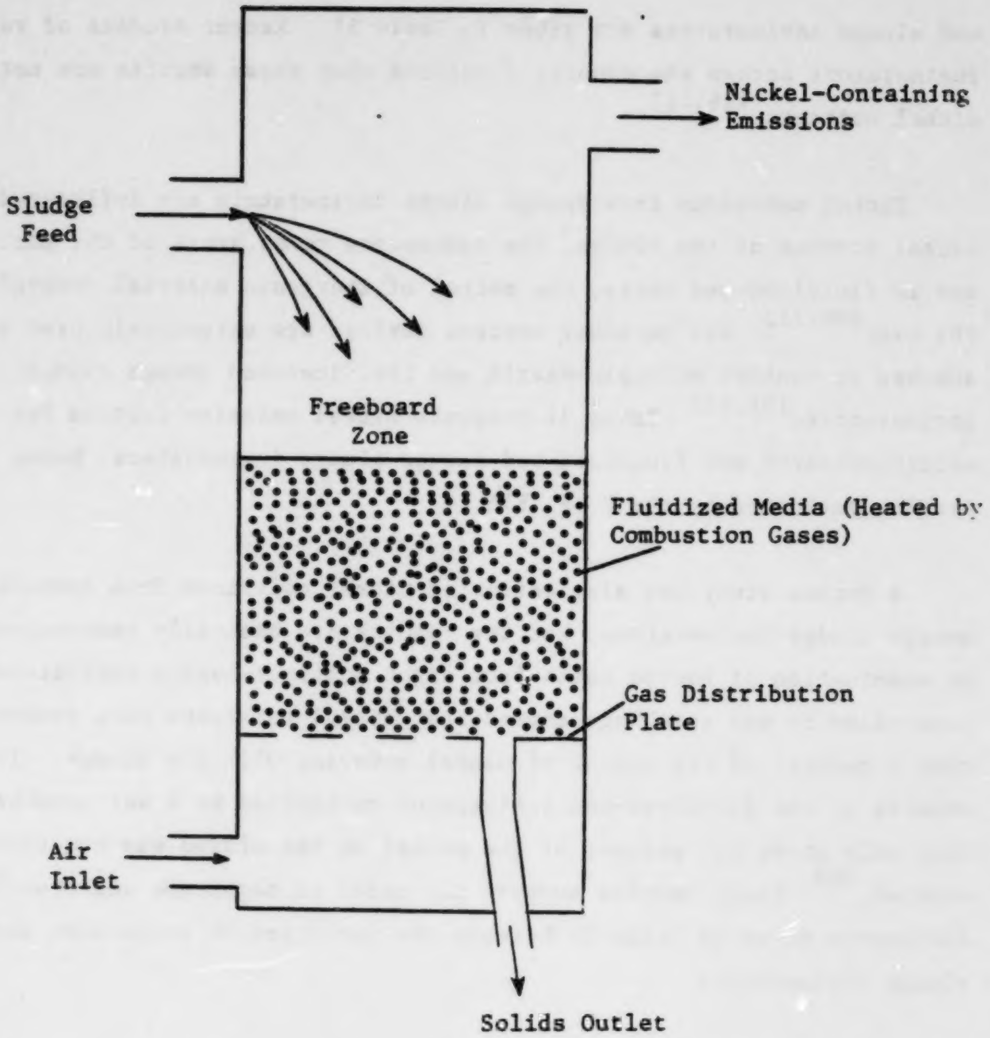
[a] Hearth 1 is at the top of the furnace and 6 is at the bottom.

The second technique used to oxidize sewage sludge is fluidized-bed incineration. Figure 23 represents the basic operations found in a fluidized-bed unit.[112] In this operation dewatered sludge is introduced into the freeboard area of the incinerator just above the fluidized bed material (which is usually sand). Hot combustion gases rising from the bed evaporate remaining water in the sludge and sludge solids and then enter the fluidized bed. The organic constituents of the sludge are oxidized to carbon dioxide and water vapor, which exit the system as exhaust gases. During this reaction, the bed is vigorously mixed and the bed temperature is maintained at 704-816°C (1300-1500°F). Remaining inorganic sludge material either deposits on the bed sand particles and is removed from the bottom of the reactor, or it can be made to exit with the exhaust gases. Air velocity through the bed is used to control the method of inorganic sludge material removal. Nickel emissions from this type of system are dependent on air flow velocity through the bed and the nickel content of the sludge.[112]

Emission Factors

The primary factors affecting nickel emissions from municipal refuse incinerators are the nickel content of the refuse and the manner in which combustion air is supplied to the combustion chambers. The manner in which air is supplied can affect the combustion temperature achieved and consequently the degree of nickel species volatilization and the level of fly ash emissions.[109,113] The types of control devices used to reduce overall incinerator particulate emissions have some effect on reducing nickel emissions. The configuration of controls found in the U. S. varies from simple settling chambers and baffle plates to more sophisticated ESP, wet scrubber, or fabric filter systems. No information was found in the literature describing the performance of municipal refuse incinerator controls on nickel emissions.

Nickel emission factors have been determined based on several U. S. EPA tests. The emission factors for nickel from municipal refuse incinerators



Nickel-Containing Emissions
Sludge Feed
Freeboard Zone
Fluidized Media (Heated by Combustion Gases)
Gas Distribution Plate
Air Inlet
Solids Outlet

Figure 23. Schematic diagram of a fluidized-bed sewage sludge incinerator.[112]

and sludge incinerators are given in Table 31. Recent studies of refuse incinerators across the country concluded that these sources are not major nickel emitters.[116,117]

Nickel emissions from sewage sludge incinerators are influenced by the nickel content of the sludge, the combustion temperature of the incinerator, and in fluidized-bed units, the method of inorganic material removal from the bed.[109,112] Wet scrubber control devices are extensively used with good success to control multiple-hearth and fluidized-bed sewage sludge incinerators.[109,112] Table 31 presents nickel emission factors for multiple-hearth and fluidized-bed sewage sludge incinerators, based on testing performed by the U. S. EPA.

A recent study has also estimated nickel emissions from controlled sewage sludge incinerators, but the results are basically semi-quantitative. An examination of source tests from eight multiple-hearth incinerators controlled by wet scrubbers showed that nickel emissions were generally less than 1 percent of the amount of nickel entering with the sludge. The test results of one fluidized-bed incinerator controlled by a wet scrubber showed that only about 0.1 percent of the nickel in the sludge was eventually emitted.[109] These results support the order of magnitude emission factor difference given in Table 31 between the two types of controlled sewage sludge incinerators.

The potential types of nickel compounds found in the emissions of refuse and sludge incinerators are related to the kinds of waste entering the incineration systems. Municipal refuse is generally high in plastics content such that chloride ions are likely to be prevalent. Sewage treatment sludge is affected by the kinds of discharges entered into the publicly owned treatment works (POTW's). Phosphates from human wastes and detergent use can be significant in sludges to be incinerated. Local industry can also greatly affect the kinds of nickel compounds found in

TABLE 31. EMISSION FACTORS FOR NICKEL FROM MUNICIPAL REFUSE AND SEWAGE SLUDGE INCINERATORS[26,114,115]

Emission Source	Nickel Emission Factor, kg/Mg (lb/ton) of Solid Waste Incinerated[a]	
Municipal Refuse Incinerators[b]		
Refuse Only[c]	0.002	(0.003)[d]
Refuse and Sludge[c]	0.003	(0.005)[d]
Sewage Sludge Incinerators[e]		
Multiple Hearth[c]	0.002	(0.003)[f,g]
Fluidized Bed[c]	0.0002	(0.0003)[g,h]
Uncontrolled Multiple-Hearth or Fluidized-Bed Unit	0.07	(0.15)

[a] All factors expressed in terms of total elemental nickel.

[b] Nickel emissions are expected to be in the forms of nickel chloride, nickel sulfate, and complex oxides of nickel and other metals.

[c] Source is controlled by a wet scrubber.

[d] Emission factors determined from U.S. EPA testing and analysis of one municipal incinerator.

[e] Nickel emissions are expected to be in the forms of nickel sulfate, nickel phosphate, nickel chloride, nickel nitrate, and complex oxides of nickel and other metals.

[f] Emissions found to range from 0.0003 to 0.004 kg/Mg (0.0006-0.008 lb/ton).

[g] Emission factors determined from U.S. EPA testing and analysis of three sewage sludge incinerators.

[h] Emissions found to range from 0.0001 to 0.0002 kg/Mg (0.0002-0.0003 lb/ton).

sludge, particularly if plating or nickel chemical facilities exist that discharge into POTW's.[118]

An absolute species characterization of potential nickel emissions from incinerators is difficult because the compositions of waste streams vary so greatly between units and even daily within the same unit. Recent tests, however, on the fly ash emissions of three different refuse incinerators and three different sludge incinerators have produced results that greatly aid in estimating the species of nickel potentially being emitted. Fly ash emissions from refuse and sludge incineration were determined to be one-third to one-half water soluble. The soluble phase of refuse incinerator fly ash contained principally chloride and sulfate ions.[118] The fraction of total nickel from refuse incinerator fly ashes that was water soluble ranged from less than 47 to 84 percent.[118] Nickel compounds in the water soluble phase of these emissions are probably nickel chloride and/or nickel sulfate, although this was not confirmed during these analyses. The insoluble portion of these ashes contained primarily oxide and silicate salts of various metals. Although not specifically identified, complex oxides of nickel and other metals (mainly iron) are probably the prevalent forms of nickel that would exist.

The water soluble phase of the sludge incinerator fly ash was found to contain predominantly sulfate ions, although chloride, nitrates, and phosphates were present at much lower levels. The fraction of total nickel that was water soluble in sludge incinerator fly ash ranged from 34 to 52 percent.[118] It is reasonable to expect that nickel emissions present in the water soluble phase of sludge incinerator emissions are predominantly nickel sulfate, with potentially much lesser amounts of nickel chloride, nitrate, and phosphate. The insoluble phase of sludge incinerator fly ash emissions was similar to that from refuse incinerator emissions.[111] Principally oxide, silicate, and phosphate salts of various metals were identified, such that the probability is great that nickel exists as complex oxides of nickel and other metals. It is highly likely that nickel was combined with iron to form a spinel; however, such a conclusion was not explicitly determined.

Source Locations

In 1979, there were 108 municipal refuse incinerators and 358 sewage sludge incinerators in the U. S.[119,120] Table 32 presents a breakdown of the number of incinerators of each type found by state. Additional information on the specific locations of these facilities can be obtained from the Compliance Data System maintained by U. S. EPA Regional offices.

Coke Ovens

Process Description

The production of metallurgical coke is a potential source of nickel emissions because of nickel in the coal being processed. Coke production involves the destructive distillation of coal by heating it in a low oxygen atmosphere, driving off gases generated by the decomposition of organic compounds in the coal. After distillation only the relatively involatile coke remains. The primary method of coking in the U. S. is the byproduct method, which accounts for 98 percent of domestic production.[121]

The byproduct method is designed to recover gases generated during the coking process. A coke battery comprises a series of 40 to 70 narrow rectangular, slot-type coking ovens interspersed with heating flues. Figure 24 illustrates the arrangement of a typical coke oven battery. Coal is charged into ports on the top of the ovens by a device called a larry car. After charging, the ports are sealed, and heat is supplied to the ovens by the combustion of gases passing through the flues between ovens. The fuels used in the combustion process are natural gas, coke oven gas, or gas from an adjacent blast furnace. Inside the ovens, coke is first formed near the exterior walls and then the process progresses toward the oven

TABLE 32. POPULATION OF MUNICIPAL REFUSE AND SEWAGE SLUDGE INCINERATORS IN THE UNITED STATES BY STATE IN 1978[119,120]

State	No. of Municipal Refuse Incinerators	No. of Sewage Sludge Incinerators
Alabama	0	1
Alaska	0	6
Arizona	0	0
Arkansas	0	2
California	0	18
Colorado	0	0
Connecticut	16	11
Delaware	1	0
District of Columbia	0	0
Florida	8	3
Georgia	0	8
Hawaii	0	2
Idaho	0	0
Illinois	4	6
Indiana	1	10
Iowa	0	4
Kansas	0	4
Kentucky	0	4
Louisiana	3	6
Maine	0	1
Maryland	1	7
Massachusetts	0	15
Michigan	3	55
Minnesota	0	11
Mississippi	0	0
Missouri	2	16
Montana	0	0
Nebraska	0	2
Nevada	0	3
New Hampshire	2	5
New Jersey	7	17
New Mexico	0	0
New York	31	32
North Carolina	0	5
North Dakota	0	0
Ohio	6	27
Oklahoma	0	2
Oregon	0	1
Pennsylvania	10	21
Rhode Island	1	5
South Carolina	0	3

TABLE 32. (CONTINUED)POPULATION OF MUNICIPAL REFUSE AND SEWAGE SLUDGE INCINERATORS IN THE UNITED STATES BY STATE IN 1978[119,120]

State	No. of Municipal Refuse Incinerators	No. of Sewage Sludge Incinerators
South Dakota	0	0
Tennessee	2	9
Texas	0	9
Utah	2	0
Vermont	0	0
Virginia	2	15
Washington	0	5
West Virginia	0	3
Wisconsin	4	4
Wyoming	0	0
TOTAL	108	358

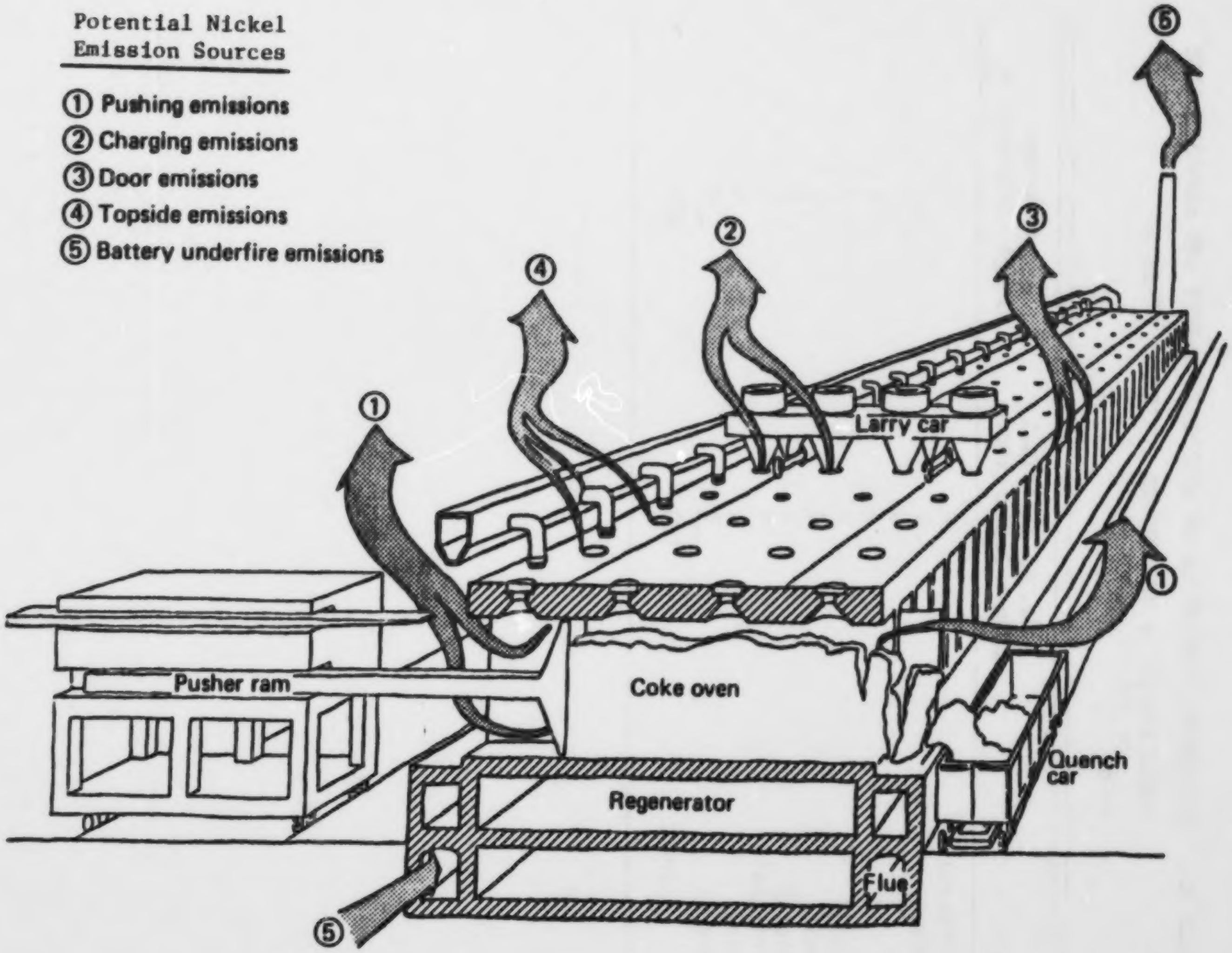

Potential Nickel Emission Sources
① Pushing emissions
② Charging emissions
③ Door emissions
④ Topside emissions
⑤ Battery underfire emissions
⑤
③
②
④
①
Larry car
①
Pusher ram
Coke oven
Quench car
Regenerator
Flue
⑤

Figure 24. Metallurgical coke oven battery.[121]

center, where temperatures of 1150°C (2100°F) can be reached. The complete coking process takes 16 to 20 hours. Once the process is complete, coke is removed from the oven simply by pushing it out with a ram into a quenching car. The quenching car full of extremely hot coke is moved into the quench tower and cooled by applying several thousand gallons of water. The coke is then allowed to dry before being separated into various size fractions for future uses.[121]

Emission Factors

The possible process related nickel emission points from a coke oven battery are indicated in Figure 24. Nickel emissions may also be generated during quenching operations and from materials handling operations involving coal unloading, crushing, and sizing.[121] The form of nickel emissions from these coking sources has not been determined and expressed in the literature.

Only one emission factor for nickel from metallurgical coke production is available from the literature. The level of uncontrolled nickel emissions from coke ovens are estimated by this factor to be 0.008 kg/Mg (0.0016 lb/ton) of coal processed.[122]

Source Locations

Table 33 presents the complete listing of coke production plants in the United States as of January 1980.[123]

Asbestos Mining

The mining and milling of asbestos minerals such as chrysotile can be a potential source of nickel emissions because chrysotile contains 1.5-1.8 mg nickel/g of chrysotile. Dusts generated during the milling of chrysotile to recover asbestos fibers can therefore contain small quantities of nickel.

TABLE 33. COKE PLANTS IN THE UNITED STATES AS OF JANUARY 1980[123]

Company Name	Plant Location
Armco, Inc.	Hamilton, OH
	Houston, TX
	Middletown, OH (2)
Bethlehem Steel Corp.	Bethlehem, PA
	Burns Harbor, IN
	Johnstown, PA
	Lackawanna, NY
	Sparrows Point, MD
CF&I Steel Corp.	Pueblo, CO
Crucible Steel, Inc.	Midland, PA
Cyclops Corp. (Empire-Detroit)	Portsmouth, OH
Ford Motor Co.	Dearborn, MI
Inland Steel Co.	E. Chicago, IN (3)
Interlake, Inc.	Chicago, IL
J&L Steel Corp.	Aliquippa, PA
	Campbell, OH
	E. Chicago, IN
	Pittsburgh, PA
Kaiser Steel Corp.	Fontana, CA
Lone Star Steel Co.	Lone Star, TX
National Steel Corp.	Granite City, IL
	Detroit, MI
	Weirton, WV
	Brown's Island, WV
Republic Steel Corp.	Cleveland, OH (2)
	Gadsden, AL
	Massillon, OH
	S. Chicago, IL
	Thomas, AL
	Warren, OH
	Youngstown, OH
U. S. Steel Corp.	Clairton, PA (3)
	Fairfield, AL

TABLE 33. (CONTINUED) COKE PLANTS IN THE UNITED STATES AS OF JANUARY 1980[123]

Company Name	Plant Location
	Fairless Hills, PA Gary, IN Lorain, OH Provo, UT
Wheeling-Pittsburgh	E. Steubenville, WV Monessen, PA
Alabama By-Products Corp.	Tarrant, AL
Allied Chemical Corp.	Ashland, KY
Carondelet Coke Company	St. Louis, MO
Chattanooga Coke and Chemical Comp.	Chattanooga, TN
Citizens Gas and Coke Utility	Indianapolis, IN
Detroit Coke	Detroit, MI
Donner-Hanna Coke Corp.	Buffalo, NY
Empire Coke Comp.	Holt, NY
Erie Coke and Chemicals	Painesville, OH
Indiana Gas and Chemical	Terre Haute, IN
Ironton Coke Corp. (McLouth Steel)	Ironton, OH
Keystone Coke Comp.	Swedeland, PA
Jim Walter	Birmingham, AL
Koppers Co., Inc.	Erie, PA Toledo, OH Woodward, AL
Milwaukee Solvay	Milwaukee, WI
Philadelphia Coke (Eastern Assoc. Coal Corp.)	Philadelphia, PA

TABLE 33. (CONTINUED) COKE PLANTS IN THE UNITED STATES AS OF JANUARY 1980[123]

Company Name	Plant Location
Shenango, Inc.	Neville Island, PA
Tonawanda Coke Co.	Buffalo, NY

[a] Numbers in parentheses indicate the number of plants at that location. If no number is indicated, only one plant exists at that location.

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consutling current listings and/or the plants themselves. The level of nickel emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

An analysis by the U. S. EPA of an asbestos mill producing 36,300 Mg (39,930 tons)/yr indicated an annual asbestos emission rate of 180 kg (396 lb). If it is assumed that the asbestos emissions contain 1.8 mg nickel/g of asbestos, an annual nickel emissions rate of 0.32 kg (0.71 lb) can be calculated. Milling dusts at the facility are controlled by a fabric filter system. A controlled nickel emission factor for asbestos milling operations, in terms of total asbestos produced, is 0.000009 kg/Mg (0.000018 lb/ton).[124,125]

Other sources of nickel emissions from asbestos operations are dry waste piles of chrysotile tailings. These tailings are generated from the asbestos fiber recovery processes. Generally, the waste piles are open and exposed to winds which can dislodge and transport nickel-containing tailings. Because the recovery efficiency of asbestos fiber from chrysotile is low (5 to 50 percent), a large amount of nickel-containing chrysotile is present in the tailings for possible wind distribution. The levels of nickel emissions from waste tailings piles have not been determined.[124,125]

Currently, there are four asbestos mining and milling operations in the United States. These operations are located in Arizona, California, and Vermont.[126]

Coal Conversion Processes

The category of coal conversion processes includes coal gasification and coal liquefaction plants. The existence of nickel compounds in the air emissions of these facilities has qualitatively been determined; however, no data are available quantifying such nickel emissions.[127] Nickel metal, nickel carbonyl, and nickel subsulfide have either been found or are suspected in several unit process emission streams from gasification and liquefaction plants.

The process flow sheets given in Figures 25 and 26 represent typical gasification and liquefaction plants. The operations within each process that are known or suspected nickel emission sources are denoted by dotted lines, and they are listed individually in Table 34. The only confirmed nickel emission sources are hydrotreating and hydrocracking operations in liquefaction plants (nickel metal emissions) and the methanation reaction operation in gasification plants (nickel carbonyl emissions). More testing and characterization of emissions from these types of facilities are required to confirm and quantify the severity of nickel emissions.

The number of gasification and liquefaction plants in the United States is relatively small. The majority of plants are demonstration or pilot scale plants geared to be research tools for a particular gasification or liquefaction technology.

Petroleum Processing

The petroleum processing category includes refineries conducting light, intermediate, and heavy hydrocarbon processing. Several sources within these hydrocarbon processing operations have qualitatively been determined to have nickel air emissions.[128] No data quantifying these emissions are available; however, nickel metal and nickel carbonyl are known or suspected to be present.

The process flow sheets given in Figures 27, 28, and 29 are basic representations of light, intermediate, and heavy hydrocarbon processing operations, showing which sources have nickel air emissions. Known and suspected nickel emission sources from all three types of hydrocarbon processing are summarized in Table 35. All three of these processing operations also have nickel emissions as a result of using oil fired process heaters. Emission factors presented in the oil combustion section are applicable to oil fired process heaters.

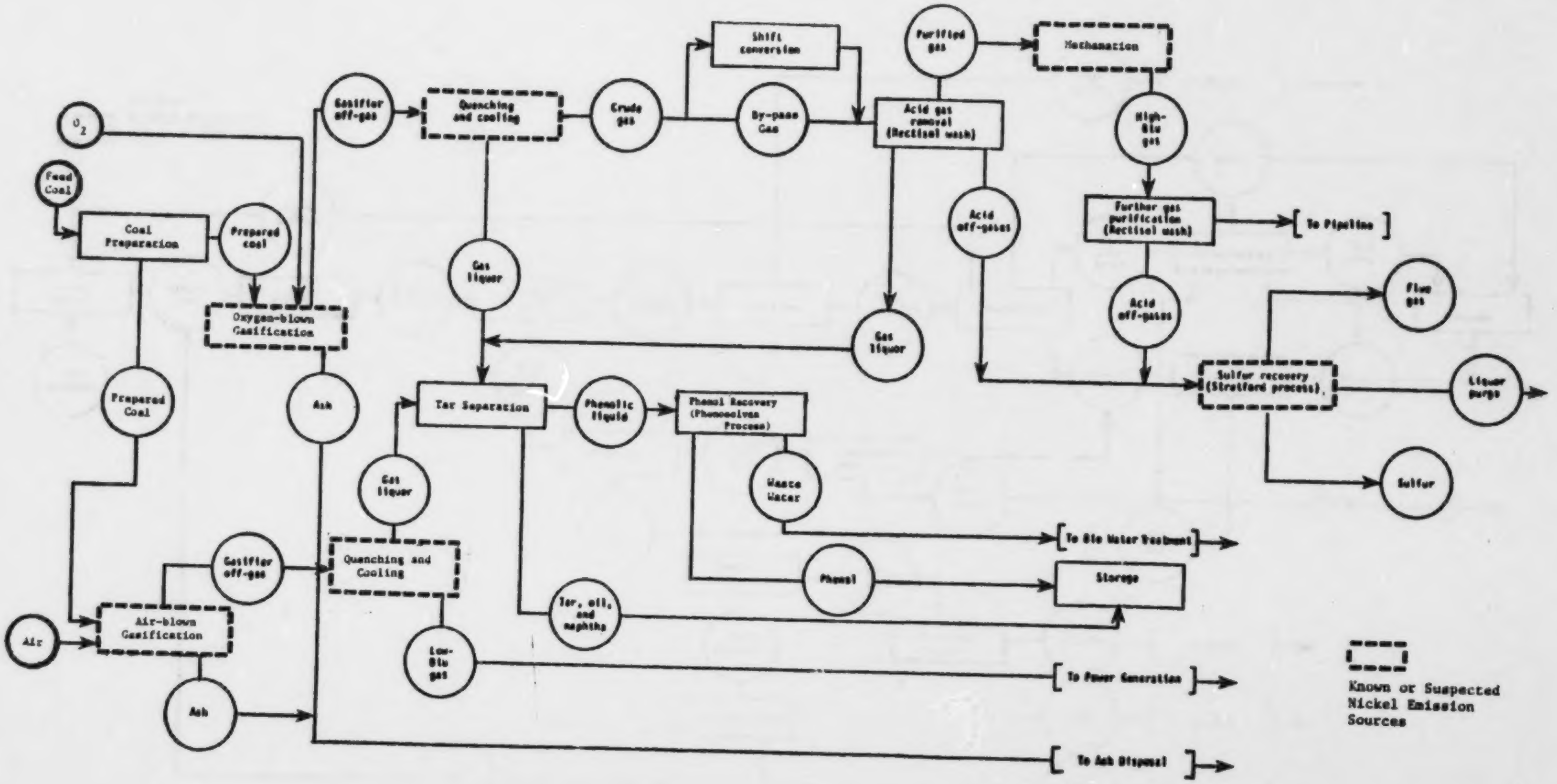

O_2
Feed Coal
Coal Preparation
Prepared coal
Oxygen-blown Gasification
Prepared Coal
Ash
Gasifier off-gas
Quenching and cooling
Crude gas
Shift conversion
By-pass Gas
Acid gas removal (Rectisol wash)
Purified gas
Methanation
High-Btu gas
Further gas purification (Rectisol wash)
To Pipeline
Acid off-gases
Gas liquor
Acid off-gases
Flue gas
Sulfur recovery (Stretford process)
Liquor purge
Sulfur
Gas liquor
Tar Separation
Phenolic liquid
Phenol Recovery (Phenosolvan Process)
Waste Water
To Bio Water Treatment
Phenol
Storage
Gas liquor
Tar, oils, and naphtha
Air
Air-blown Gasification
Gasifier off-gas
Quenching and Cooling
Low-Btu gas
To Power Generation
Ash
To Ash Disposal
Known or Suspected Nickel Emission Sources

Figure 25. Representative flow diagram for a coal gasification process.[127]

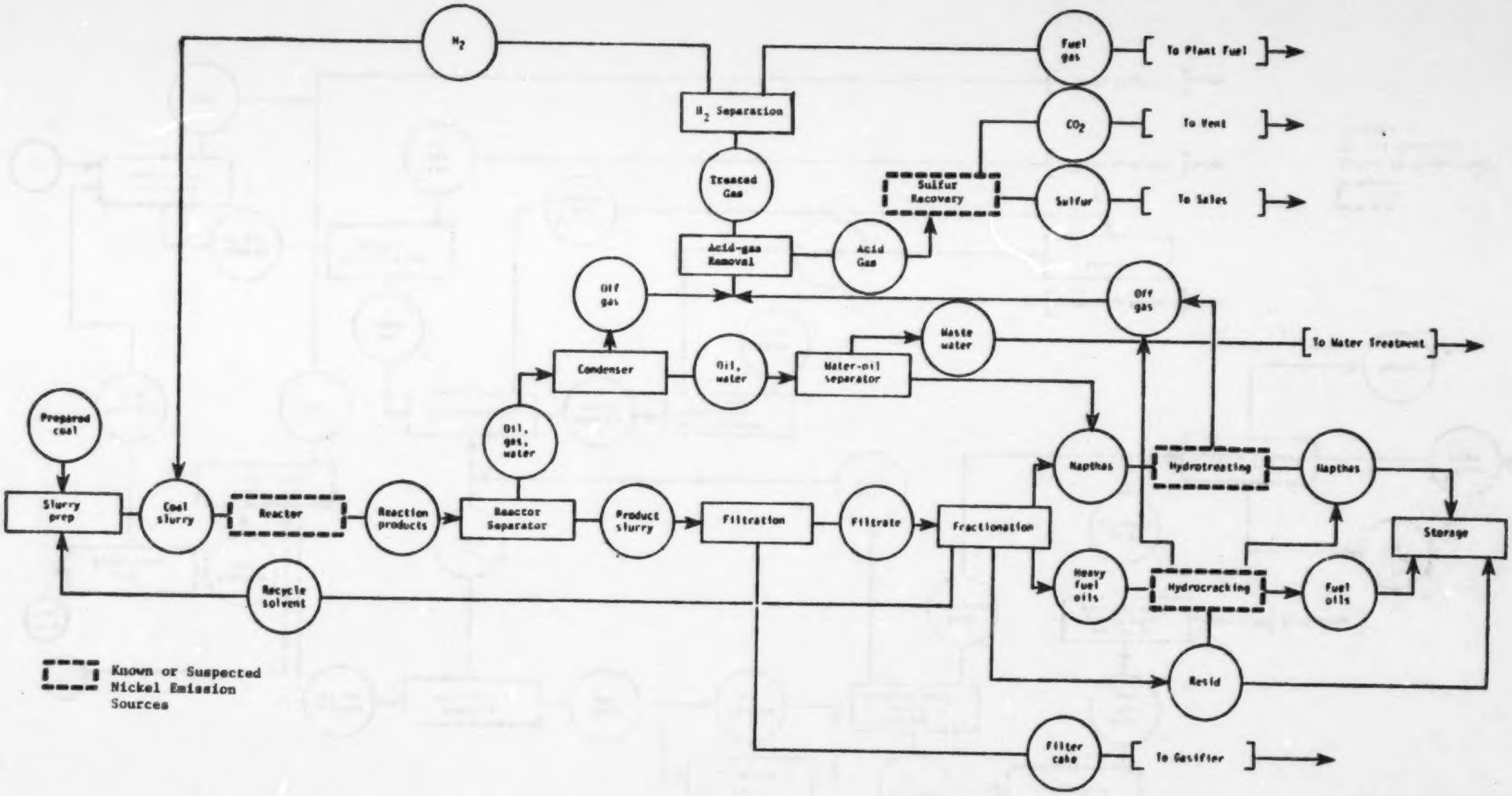

H2
H2 Separation
Fuel gas
To Plant Fuel
CO2
To Vent
Treated Gas
Sulfur Recovery
Sulfur
To Sales
Acid-gas Removal
Acid Gas
Off gas
Off gas
Condenser
Oil, water
Water-oil separator
Waste water
To Water Treatment
Prepared coal
Oil, gas, water
Slurry prep
Coal slurry
Reactor
Reaction products
Reactor Separator
Product slurry
Filtration
Filtrate
Fractionation
Napthas
Hydrotreating
Napthas
Storage
Heavy fuel oils
Hydrocracking
Fuel oils
Recycle solvent
Resid
Filter cake
To Gasifier
Known or Suspected Nickel Emission Sources

Figure 26. Representative flow diagram for a coal liquefaction process.[127]

TABLE 34. OPERATIONS WITHIN A COAL GASIFICATION AND LIQUEFACTION PROCESS THAT ARE KNOWN OR SUSPECTED NICKEL EMISSION SOURCES[127]

Coal Conversion Process	Source of Nickel Emissions	Nickel Species	Status[a]
Gasification	Quenching and Direct Cooling	Nickel Metal	Suspected
Liquefaction	Fixed-bed Catalyst Regeneration (Hydrotreating and Hydrocracking)	Nickel Metal Nickel Carbonyl	Known Suspected
Gasification, Liquefaction	Sulfur Recovery Plant	Nickel Metal	Suspected
Liquefaction	Coal Slurry Reactor	Nickel Metal	Suspected
Gasification	Oxygen Blower Gasifier	Nickel Metal	Suspected
	Methanation Reactor	Nickel Metal Nickel Carbonyl	Suspected Known
	Air-blown Gasifier	Nickel Metal	Suspected

[a] The status column refers to the designation of whether the nickel species indicated is known to exist, based on some type of test data, or is suspected to be present, based on a knowledge of process materials and conditions.

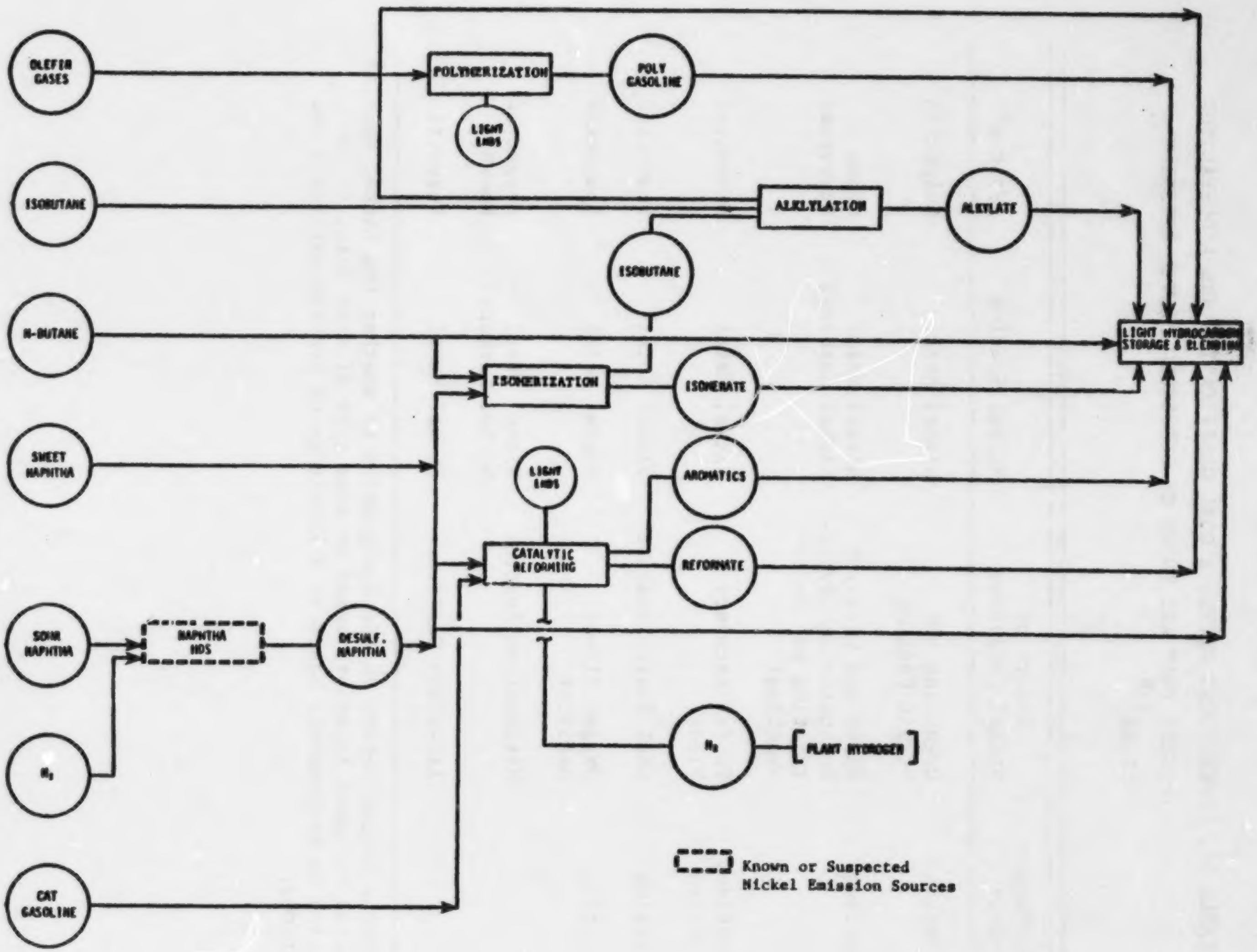

OLEFIN GASES
POLYMERIZATION
LIGHT ENDS
POLY GASOLINE
ISOBUTANE
ALKYLATION
ALKYLATE
ISOBUTANE
N-BUTANE
ISOMERIZATION
ISOMERATE
LIGHT HYDROCARBON STORAGE & BLENDING
SWEET NAPHTHA
LIGHT ENDS
AROMATICS
CATALYTIC REFORMING
REFORMATE
SOUR NAPHTHA
NAPHTHA HDS
DESULF. NAPHTHA
H2
H2
PLANT HYDROGEN
CAT GASOLINE
Known or Suspected Nickel Emission Sources

Figure 27. Typical flow diagram for a light hydrocarbon processing facility.[128]

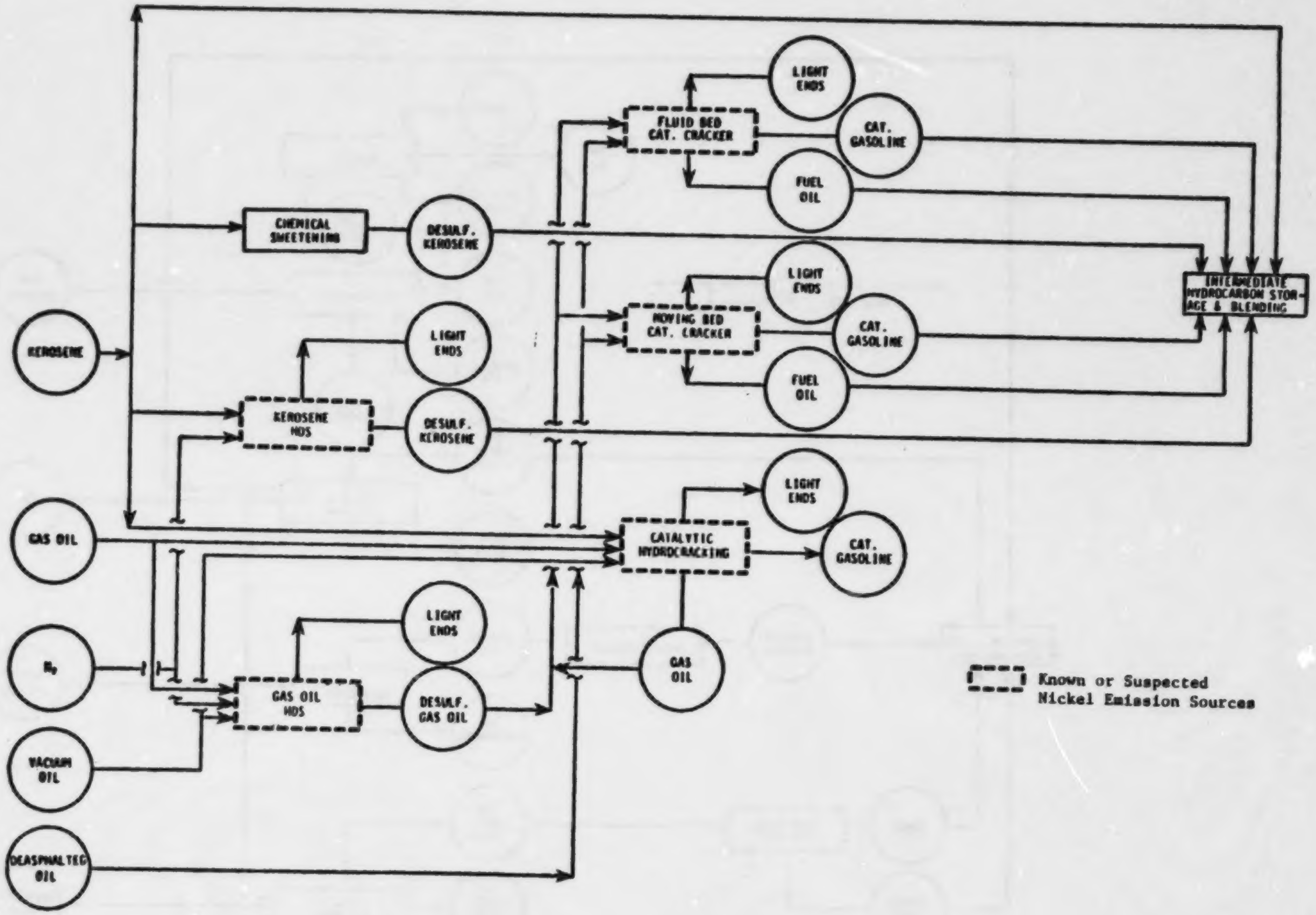

KEROSENE
GAS OIL
H_2
VACUUM OIL
DEASPHALTED OIL
CHEMICAL SWEETENING
DESULF. KEROSENE
KEROSENE HDS
LIGHT ENDS
DESULF. KEROSENE
GAS OIL HDS
LIGHT ENDS
DESULF. GAS OIL
FLUID BED CAT. CRACKER
LIGHT ENDS
CAT. GASOLINE
FUEL OIL
MOVING BED CAT. CRACKER
LIGHT ENDS
CAT. GASOLINE
FUEL OIL
CATALYTIC HYDROCRACKING
LIGHT ENDS
CAT. GASOLINE
GAS OIL
INTERMEDIATE HYDROCARBON STORAGE & BLENDING
Known or Suspected Nickel Emission Sources

Figure 28. Typical flow diagram for an intermediate hydrocarbon processing facility.[128]

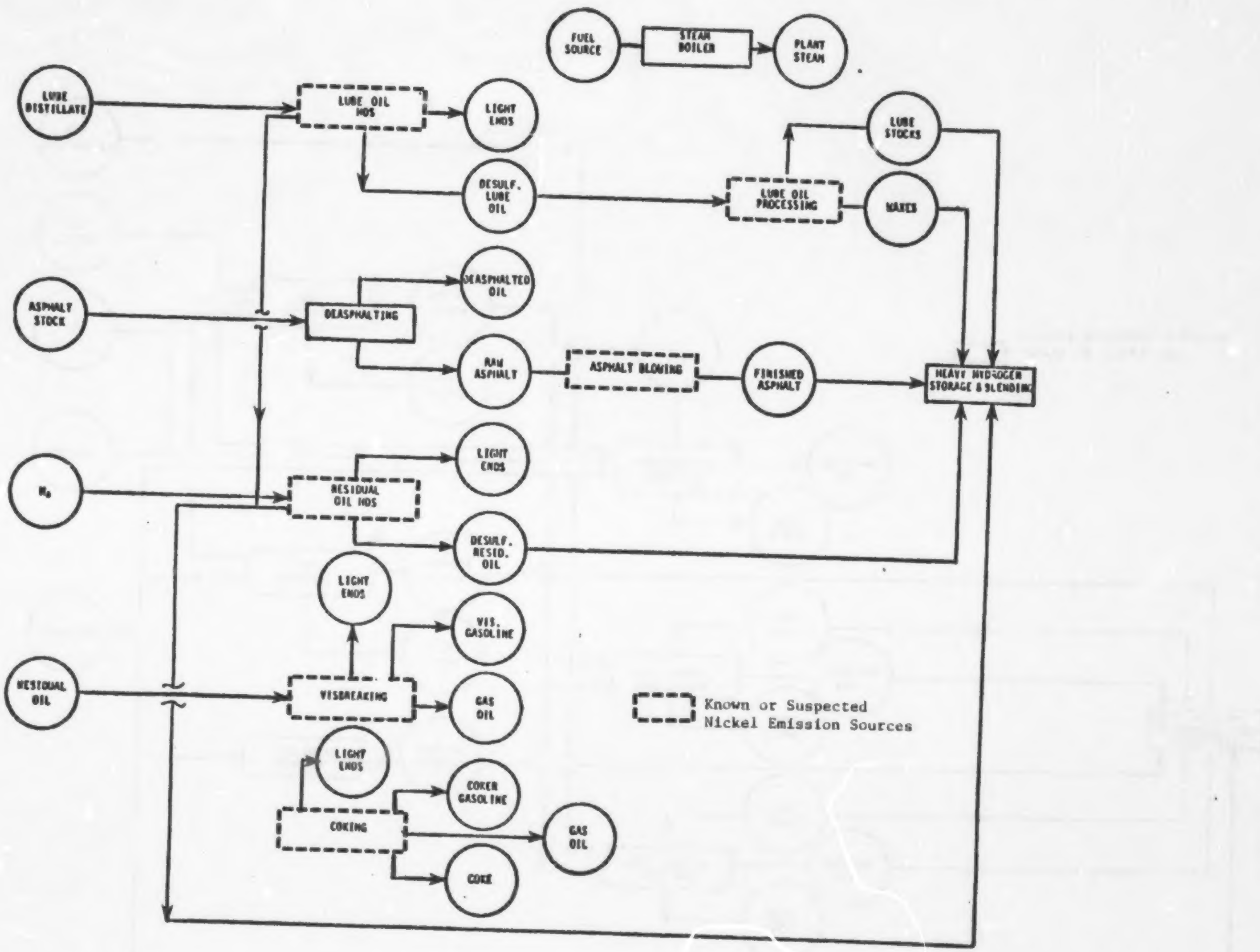

FUEL SOURCE
STEAM BOILER
PLANT STEAM
LUBE DISTILLATE
LUBE OIL HDS
LIGHT ENDS
DESULF. LUBE OIL
LUBE OIL PROCESSING
LUBE STOCKS
WAXES
ASPHALT STOCK
DEASPHALTING
DEASPHALTED OIL
RAW ASPHALT
ASPHALT BLOWING
FINISHED ASPHALT
HEAVY HYDROGEN STORAGE & BLENDING
H2
RESIDUAL OIL HDS
LIGHT ENDS
DESULF. RESID. OIL
LIGHT ENDS
VIS. GASOLINE
RESIDUAL OIL
VISBREAKING
GAS OIL
Known or Suspected Nickel Emission Sources
LIGHT ENDS
COKER GASOLINE
COKING
GAS OIL
COKE

Figure 29. Typical flow diagram for a heavy hydrocarbon processing facility.[128]

TABLE 35. KNOWN OR SUSPECTED NICKEL EMISSION SOURCES WITHIN LIGHT, INTERMEDIATE, AND HEAVY HYDROCARBON PROCESSING OPERATIONS[128]

Source of Nickel Emissions	Nickel Species	Status[a]
Light Hydrocarbon Processing		
Naphtha Hydrodesulfurization[b]	Nickel Metal Nickel Carbonyl	Known Suspected
Intermediate Hydrocarbon Processing		
Kerosene Hydrodesulfurization[b]	Nickel Metal Nickel Carbonyl	Known Suspected
Gas Oil Hydrodesulfurization[b]	Nickel Metal Nickel Carbonyl	Known Suspected
Fluidized-bed Catalytic Cracker	Nickel Metal	Known
Moving-bed Catalytic Cracker	Nickel Metal	Known
Catalytic Hydrocracking	Nickel Metal Nickel Carbonyl	Known Suspected
Heavy Hydrocarbon Processing		
Lube Oil Hydrodesulfurization[b]	Nickel Metal Nickel Carbonyl	Known Suspected
Residual Oil Hydrodesulfurization[b]	Nickel Metal Nickel Carbonyl	Known Suspected
Lube Oil Processing	Nickel Metal Nickel Carbonyl	Known Suspected
Fluid Coker Offgas	Nickel Metal	Known
Decoking-Visbreaking	Nickel Metal	Known
Asphalt Air Blowing	Nickel Metal	Known

[a] The status column refers to the designation of whether the nickel species indicated is known to exist, based on some type of test data, or is suspected to be present, based on a knowledge of process materials and conditions.

[b] While hydrodesulfurization processes may use nickel-containing catalysts, nickel emissions would not be expected to be emitted during normal operation. These processes are totally enclosed systems operating at elevated temperatures and pressures. The only possible sources of nickel emissions from these processes would be fugitive catalyst dust emissions during catalyst loading or unloading operations, which occur only once every 2 to 3 years. These operations are normally conducted so as to control dust emissions and thus limit worker exposure.[81]

As of January 1, 1982 there were 273 active refineries in the United States. Although 39 states have refineries, almost 50 percent of the total number are located in three states, California, Louisiana, and Texas.[129] A complete listing of all domestic refineries and their capacities is given in Reference 129.

Coal and Oil Supplying

This category of nickel emission sources consists of processes or operations associated with supplying coal and oil to consumers. For the supply of coal, operations such as extraction, transportation, preparation, distribution, and storage constitute the primary sources of nickel emissions. Extraction operations consist of underground, surface (basically strip), and auger (another form of surface mining) mining. Transportation operations include hauling the coal from the mining site to the coal preparation site. Trucks, rail cars, and conveyors are predominantly used for this purpose. The type of transportation used is generally dependent on the type of mining being conducted. Trucks are used primarily at surface and auger mines, while rail cars and conveyors are used at underground mining sites.

Once transported to a preparation site, coal can be processed in a variety of ways including:

- crushing and screening to a maximum desired size,
- cleaning to remove dust and non-coal material, and
- drying to prepare the coal for shipment or use.

The particular chemical and physical characteristics of a coal dictate the amount of preparation required.

Distribution operations involve the shipment of coal from the preparation site to the point of consumption. Rail cars, barges, trucks, slurry pipelines, and conveyors are the predominant means of coal distribution. Lastly, storage operations involve the open storage of coal in piles or the storage of coal in enclosed silos or bins at the consumption site.[130]

Nickel emissions from coal supplying activities occur as part of the dusts associated with the coals. Nickel emissions from coal dusts vary by region of the country because coal nickel content varies by region (see Table 23). Most emissions of this type are fugitive in nature and result from wind action on the coal piles and coal loading/unloading activities. No nickel emissions or emission factor data have been developed for these fugitive sources. Nickel emissions may also occur due to nickel-containing oil products being burned to power trucks, trains, barges, and other heavy equipment used to supply coal.[130] Emission factors and national emissions associated with the combustion of oil and petroleum products are discussed in the section entitled, Coal and Oil Combustion.

The process of supplying oil has many of the same nickel-emitting operations as supplying coal, including extraction, transportation, distribution, and storage. Oil processing or refining operations are also a component of the oil supply matrix; however, nickel emissions associated with these operations have been discussed in a previous section entitled Petroleum Processing. The remaining oil supply nickel-emitting operations are briefly described below.

In the supply of oil, extraction refers to onshore or offshore drilling operations. Transportation involves moving the oil from the drilling site to the processing or refining site. Pipelines, tankers, and barges are used for this purpose. Oil distribution from the processing site to the consumption market is generally accomplished by pipeline, barge, or tank truck. Oil supply storage operations refer to the storage of crude oil or refined oil products in tanks. Storage activities can occur at the refining site and at the site of product consumption.[130]

Nickel emissions from supplying oil and oil products result mainly from fuel combustion in trucks, barges, and other equipment used in extraction, transportation, and distribution operations. Again, nickel emissions of this type have been previously considered in the section, Coal and Oil Combustion.

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SECTION 5

SOURCE TEST PROCEDURES

Specific sampling and analysis source test procedures have not been published by the U. S. EPA for suspected nickel emissions sources. The sampling and analysis methods presented in this section represent a collection of nickel air emission detection and quantification techniques that have been published in the open literature as viable methods. The presentation of these published methods in this report does not constitute endorsement or recommendation or signify that the contents necessarily reflect the views and policies of the U. S. EPA.

LITERATURE REVIEW OF SAMPLING METHODS

Trace amounts of nickel can be determined using a sampling train developed by Hamersma, et al.[1,2] This system is designed to sample under high pressure environments under isokinetic conditions. The sampling train consists of (1) a modified ASTM liquid sampling probe, (2) an impinger for condensing water and oil vapors in an ice bath under pressure, (3) a pressure reduction mechanism, and (4) a second impinger series where nickel and its compounds are expected to be found. The contents of the second set of impingers are: 3M H_2O_2 in the first; 3M H_2O, 0.2 M $(NH_4)_2S_2O_8$, and 0.02 M $AgNO_3$ in the second and third; and Drierite for drying the sampling gases in the fourth. The sampling train is capable of operating at temperatures up to 500°C (932°F) and pressures greater than 2000 kPa (300 psig). Sampling rates of 2 to 10 m^3 (71-353 ft^3) of gas over a 1 to 4 hour period are used. The detection limit for nickel in a gas stream is 60 $\mu g/m^3$.

A similar system for flue gas sampling for trace inorganic materials at atmospheric pressures was designed by Flegal, et al.[1,3] The sampling train consists of a standard Aerotherm high volume stack sampler (HVSS) modified in three areas: (1) the probe is lined with a removable inner liner made of Kapton polyimide film to prevent nickel, chromium, and other components in the stainless steel probe from contaminating the particulate catch; (2) a Gelman Spectrograde type A glass fiber filter is used as the filtering medium, and (3) a special oxidative impinger system is used to sample vapors. The oxidative system consists of four impingers: one impinger with 3M H_2O_2, two impingers with 0.2 M $(NH_4)_2S_2O_8$ plus 0.02 M $AgNO_3$, and a fourth impinger with Drierite. The impinger nozzles are coated with Teflon to prevent corrosion of the stainless steel components due to the oxidative solutions. The system is designed to operate in a flue gas stream at temperatures up to 270°C (518°F) and a sampling rate of up to 90 liters per minute (3 cfm).

EPA Method 5, as modified effective September 19, 1977, has been used to sample nickel dust.[4] This train consists of the following components: a stainless steel or glass probe nozzle with an appropriate liner (e.g., borosilicate or quartz glass) capable of maintaining a gas temperature at the exit of 120°C ± 14°C (248°F ± 57°F), an S type pitot tube, a differential pressure gauge, a borosilicate glass filter holder, a filter heating system capable of maintaining a temperature of 120°C ± 14°C during sampling, and a condenser system consisting of four impingers for determining the stack gas moisture content. The first and second impingers in the condenser system are of the modified Greenberg-Smith design and contain known amounts of water; the third is the same design but empty; and the fourth is a regular Greenberg-Smith impinger filled with a desiccant (silica gel, calcium sulfate, or any other appropriate material). The system also includes a metering system consisting of a vacuum gauge, leak-free pump, thermometer, and a volume measuring gas meter, a barometer, and gas density determination equipment. The sample is recovered from the system by washing the nozzle and probe liner with acetone and combining the wash eventually with the particulate matter collected on the filter and filter holder.

- Peters, et al. proposed and tested a sampling train similar to Method 5 for particulate sampling.[5] This system is all glass in order to avoid metal contamination. Stack emissions are isokinetically sampled from the source at an appropriate rate [(0.014-0.028 m^3/min), (0.49-0.99 ft^3/min)] and for a sufficient period to collect a 24-hour representative sample (recommended minimum sampling period is 2 hours). The main components in the system are a stainless steel or glass nozzle with sharp, tapered leading edge; a sheathed borosilicate glass probe with a heating system capable of maintaining a minimum gas temperature in the range of the stack temperature; a pitot tube type S, or equivalent, attached to probe to monitor stack gas velocity; a differential pressure gauge to measure velocity head to within 10 percent of the minimum value; a filter holder made of borosilicate glass; four Greenberg-Smith impingers; a metering system; and a barometer. The first two impingers contain 0.1 M nitric acid, the third impinger is left empty, and the fourth contains 200 g (0.44 lb) of preweighed silica gel. The filter is a high efficiency Gelman Microquartz fiber filter (99.95 percent efficiency on 0.3 dioctyl phthalate smoke particles.)

EPA Level 1 Environmental Assessment Flue Gas Sampling Trains (SASS) has been the most widely used system for sampling inorganics, including nickel and nickel compounds.[6] It is mainly designed to collect large quantities of particulate matter, size classified in the ranges of > 10μ, 3-10μ, 1-3μ and 1μ in diameter, as well as inorganic volatile species that can be liquid absorbed. The sampling train consists mainly of a stainless steel probe, which enters an oven module containing the three size fractionating cyclones and a filter, an impinger system containing $(NH_4)_2S_28$, $AgNO_3$, high purity water and H_2O_2, and a high volume vacuum pump. It is designed to operate up to 205°C (401°F) in flue gas streams and to operate unattended.

A high-volume filtration sampler used by the National Air Sampling Network was found to be applicable for particulate sampling, but does not catch volatile compounds like nickel carbonyl.[7]

LITERATURE REVIEW OF ANALYTICAL PROCEDURES

Nickel can be detected colorimetrically using dimethylglyoxime as the complexing agent.[8] West, _et al_. adapted the ring-oven technique for the determination of nickel particulates using dimethylglyoxime as the complexing agent.[9] Neutron activation analysis (NAA) is used to determine nickel levels at the microgram level, and has a detection limit of 0.7 μg.[10] Atomic absorption spectrophotometry (without flame) (AAS) or X-ray fluorescence spectrometry (XRF) have even lower detection limits. X-ray fluorescence spectrometry is fast and has a detection limit of 0.01 $\mu g/cm^2$.[11] Flame Emission Spectrophotometry (FES) is also used, and capable of detecting 0.03 μg/ml nickel in solution.[12]

Atomic Absorption Spectrophotometry with flame (AAF) is by far the most popular technique for measuring nickel in solution. The reported detection limit is 0.005 μg/ml,[12] and the linear range for accurate measurement is reported as 0.2-5 μg/ml at a 232.0 nm wavelength setting and an oxidizing air/acetylene flame are used.[13] In a 10 ml sample, the mass required for accurate measurement is 2.50 μg. The analysis by AAF is especially appropriate for nickel because there are no known interferences. However, it was reported that a hundred fold excess of iron, manganese, chromium, copper, cobalt or zinc may decrease the absorbance recorded for nickel by as much as 12 percent.[14] Proper burner elevation and use of an oxidizing flame can minimize this effect. High solids content in the aspirated solution will cause increased nonspecific absorbance at the 232 nm line setting.[14] Thompson, _et al_.[15] reported that the National Air Pollution Control Administration found that the minimum detection limit for nickel by AAS is 0.004 $\mu g/m^3$ based on a 2,000 m^3 (70,600 ft^3) air sample.

Inductively coupled argon plasma (ICAP) has gained prominence recently as a fast and reliable analytical tool for nickel determination when multi-element analysis is required.[16] The detection limit using the 231.6 nm line is 15 μg/l.[17]

For the determination of volatile nickel carbonyl, Brief, et al. has described the following methods:[18]

(1) An air sample can be drawn through a saturated solution of sulfur in trifluoroethylene. The sulfur reacts with nickel to form a precipitate. Spectrographic examination is sensitive to 0.0003 ppm nickel carbonyl.

(2) An air sample may be drawn through a tube containing red mercuric oxide at 200°C (392°F), and the liberated mercury may be determined spectrographically. A parallel stream of air is drawn through an oxidizing reagent to convert the CO to CO_2, and the stream is passed over mercuric oxide; the liberated mercury is again determined spectrographically. The difference in the amounts of mercury vapor measured corresponds to the nickel carbonyl content in the air. A sensitivity of 0.0014 ppm is reported.

(3) Nickel carbonyl may be absorbed in chloramine. The nickel determination is accomplished colorimetrically using dimethylglyoxime. For a 30-minute sample, at the suggested sampling rate of 0.5 liters per minute, a sensitivity of 0.01 ppm is obtained.

(4) Another colorimetric method uses iodine in carbon tetrachloride as the collection medium. The nickel is colored with dimethylglyoxime. A sensitivity of 0.1 ppm to nickel carbonyl is claimed.

(5) Nickel carbonyl may be collected in dilute sulfuric acid followed by spectrophotometry using sodium diethyl-dithiocarbamate as the coloring agent.

(6) Nickel carbonyl may be collected in dilute hydrochloric acid in a midget impinger [0.0028 m^3/min (0.1 ft^3/min) for 30 minutes]. The

nickel is complexed with alpha-furildioxime and extracted with chloroform, and the content is determined spectrophotometrically. The method is sensitive to 0.0008 ppm.

A field method described by Kobayashi appears to be appropriate for analysis of nickel carbonyl in a sampling train.[19] The sample is drawn through a tube filled with silica gel impregnated with 0.5 percent gold chloride. In the presence of nickel carbonyl, the silica gel changes from light yellow to bluish-violet. The concentration of nickel carbonyl is a function of the length of the colored layer. The useful range of a 100 ml sample is 200 to 600 ppm. By measuring the minimum volume of test gas needed to color the silica gel at a constant sampling rate, the concentration of nickel carbonyl to 3 ppm can be determined.

In another method, the test air is drawn at 0.5 liter per minute through an absorption tube containing two 15 mm diameter filter papers and then through two absorption vessels with porous plates.[20] Each plate contains 3 ml of a 1.5 percent solution of chloramine-B in alcohol. The chloramine-B solution retains the nickel carbonyl vapor. The colored vapor is compared with standards. The sensitivity of the method is 1 g of nickel carbonyl, and the error does not exceed 10 percent.

SUGGESTED SAMPLING AND ANALYTICAL PROCEDURES

The modified EPA Method 5 combined with atomic absorption with flame is the suggested approach because:[5]

- The sampling train is capable of collecting both the volatile and nonvolatile nickel compounds.
- Based on nine replicate experiments the precision of the nickel measurement is 11.4 percent and the accuracy 3.9 percent at about 100 μg level.

- The quartz filter used is effective in trapping nickel particulate.
- The impinger system (0.1 M HNO_3) is appropriate for nickel sampling and allows for modification without additional cost if special trapping solutions are to be used for organometallic components.
- AAF detection method is interference free and accurate for nickel analysis using air/acetylene and the 232.0 nm line.

Reference 21 cautions that if nickel-containing particulate matter originates from high temperature processes, they are likely to be very refractory, in which case, nitric acid alone is not an adequate treatment. Perchloric acid or a fusion is often required to get high nickel recovery.

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